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PRECONCENTRATION OF TRACE ORGANIC COMPOUNDS FROM LARGE VOLUMES OF WATER

Workshop Proceedings

Canada Centre for Inland Waters
Burlington, Ontario
June 23rd, 1987

Organized by :

Water Quality Branch
and the
National Water Research Institute

Additional copies of this publication can be obtained from:

Dr. John Lawrence, National Water Research Institute, Environment Canada, P.O. Box 5050, Burlington, Ontario, Canada, L7R 4A6.

Dr. Adrian Demayo, Water Quality Branch, Environment Canada, Ottawa, Ontario, Canada, K1A 0H3.

ABSTRACT

This publication is a collection of papers discussing various techniques for liquid-liquid and solid-liquid preconcentration of organic substances from large volumes of water for subsequent chemical analysis. The presentations were followed by a discussion on the advantages and disadvantages of various techniques. In addition to a summary of the discussion, these "Proceedings" also contain a section on "Conclusions and Recommendations" related to most appropriate use of the liquid-liquid and solid-liquid techniques in water quality monitoring as well as future research in this area.

In memoriam - Dr. Peter D. Goulden

We were shocked and saddened by the death of Dr. Peter D. Goulden before the publication of these proceedings. Peter's recent work on liquid-liquid extraction and his development of the large-volume extractor for trace analysis of environmental samples is undoubtedly one of the highlights of his career. It is fitting that his last scientific presentation, at the workshop on Preconcentration of Trace Organic Compounds from Large Volumes of Water, was on this subject.

During his outstanding career, Peter made many valuable contributions to analytical chemistry research, and his achievements and reputation have been recognized worldwide. Examples of his impact on environmental analytical chemistry include his book "Environmental Pollution Analysis" and his contributions to the Water Quality Branch Analytical Methods Manual and the Analytical Protocol for Monitoring Ambient Water Quality of the Niagara River.

He is survived by his wife, Heather, four sons, and a daughter.

PROCEEDINGS

WORKSHOP ON PRECONCENTRATION OF TRACE ORGANIC COMPOUNDS FROM LARGE VOLUMES OF WATER

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INTRODUCTION

During the last 15-20 years various techniques have been evaluated for extracting organic pollutants from water including activated carbon, urethane foams, XAD resins and liquid-liquid partitioning. Of these, the last two have received the most attention because of their higher and more uniform recoveries.

With the concern for, and desire to measure, ultra trace levels (ng-pg/L) of contaminants in the aquatic environment, it became necessary to extract larger (up to 200 L) volumes of water in order to have an extract containing enough of the analyte so that it could be measured with the desired level of confidence. This led to new demands on extraction methods and required considerable scale-up of the equipment. Resin columns have become larger to prevent or diminish breakthrough, while liquid-liquid extractors have been increased in size from the conventional 1-2 L separatory funnel to devices such as the 200 L Aqueous Phase Liquid Extractor (APLE) for batch extraction, or the converted continuous flowthrough systems.

The purpose of the workshop was to convene a group of invited scientists to discuss the principles and applications of XAD resins and liquid-liquid extraction of organic contaminants from large volumes of water (surface water, ground water, drinking water and precipitation) and recommend the preferred method for different applications. Participants

were drawn from Canadian and U.S. government agencies, universities and the private sector, and included representatives of the research community, instrument manufacturing and user groups.

The formal program consisted of three review presentations covering liquid-liquid and solid-liquid extraction of surface waters and precipitation, and seven presentations of specific applications. Following the presentations an extended discussion period was held.

Abstracts of the presentations and a synopsis of the discussion period are reported in these proceedings.

The "Conclusions and Recommendations" start on page 85.

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LIQUID-LIQUID EXTRACTION

P.D. Goulden

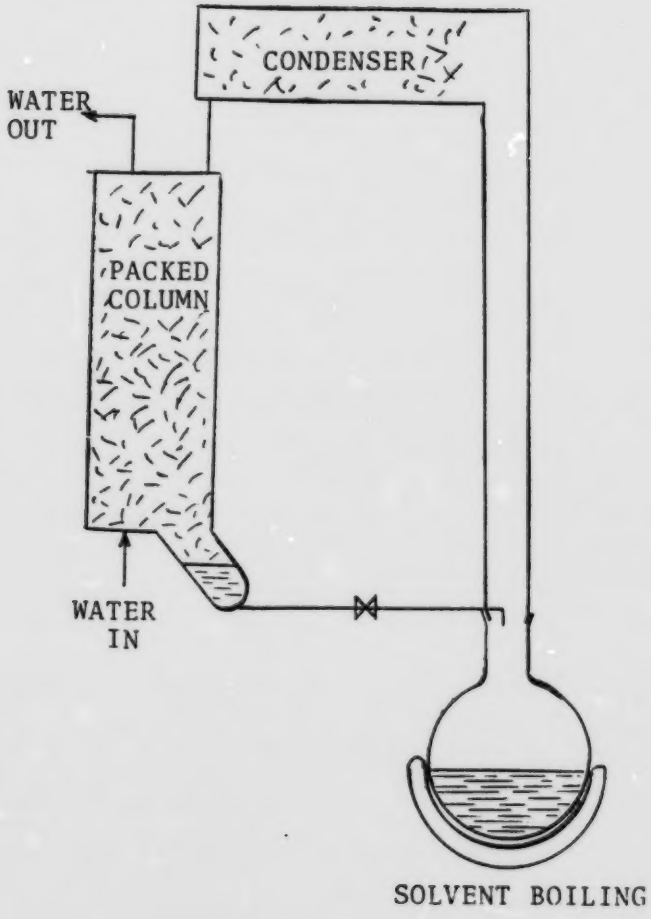
National Water Research Institute

Inland Waters/Lands Directorate

The present work on the development large-sample extractor began in 1984 with a request from Water Quality Branch, Ontario Region (WQB-OR). This request was for an extractor suitable for use on shipboard and that would be more convenient than the APLE.

The first extractor developed used a packed column in which the water was extracted by a counter-current flow of solvent. The solvent, separated at the bottom of the column, was recycled to the top of the column by distilling it. The organics extracted accumulated in the distillation pot. This work showed that although the organics could readily be extracted, the solvent recycling system would hinder the use of the equipment in the field.

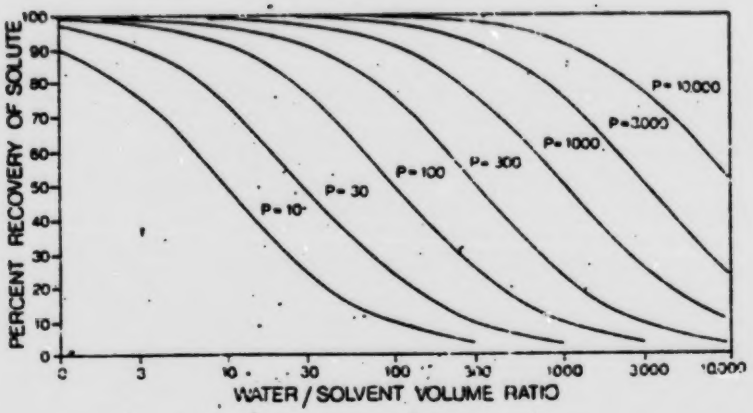
At this stage discussion were held with the WQB-OR and the Water Quality National Laboratory (WQNL) as to which organics were of interest, the volume of water that was considered to be adequate (50 L) and the volume of solvent desirable from a laboratory handling point of view (200 mL). The values reported in the scientific literature for the partition coefficient for the octanol/water system for the organics of



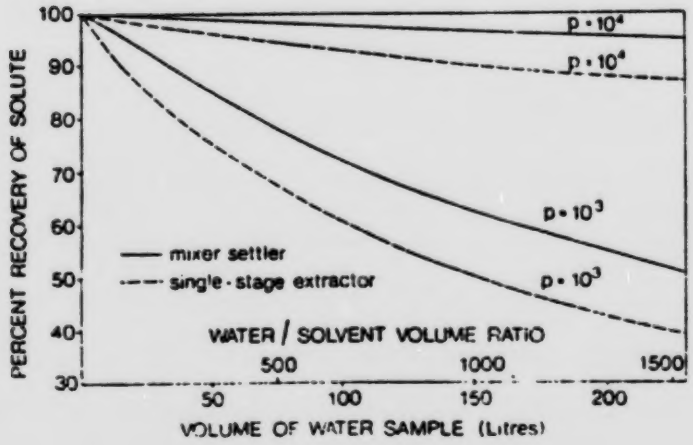
Initial liquid-liquid
extractor

interest were collated. (There are very few values reported for the dichloromethane (DCM)/water system used in the extractor). A partition coefficient of 10^4 was chosen as the basis for designing a liquid-liquid extractor. Thus from a thermodynamic point of view it was possible to extract with good efficiency 50 L of water with 200 mL DCM in a single-stage extractor. Other considerations, such as prevention of emulsions, the kinetics of the extraction and extraction of the colloidal and particulate materials demanded, however, that at the extraction stage a high solvent to water ratio be used, ideally the solvent being the continuous phase.

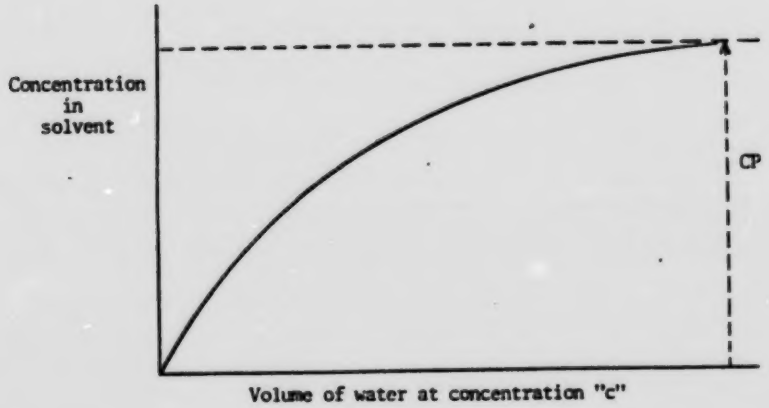
A mixer-settler type of extractor was developed. Calculations, confirmed by the high extraction efficiencies achieved in practice, showed that solvent recycling was not necessary. In this equipment the water and the solvent are circulated around an extraction loop. Care is taken to avoid any high-shear conditions that would promote emulsion formation. The settled water leaves the equipment passing up through a small column packed with "Teflon" Raschig rings. This column coalesces any small drops of solvent and breaks any emulsion formed. The solubility of DCM in water is about 1.5% by volume and, if this solvent is not recovered, it is replaced by a corresponding amount of solvent pumped in at the top of the packed column. Thus the water leaving the settler portion of the equipment is scrubbed with a low flow of clean solvent. If a solvent recovery system is used, then the recovered



EXTRACTION EFFICIENCY OF SINGLE - STAGE EXTRACTOR



EXTRACTION EFFICIENCY OF MIXER - SETTLER

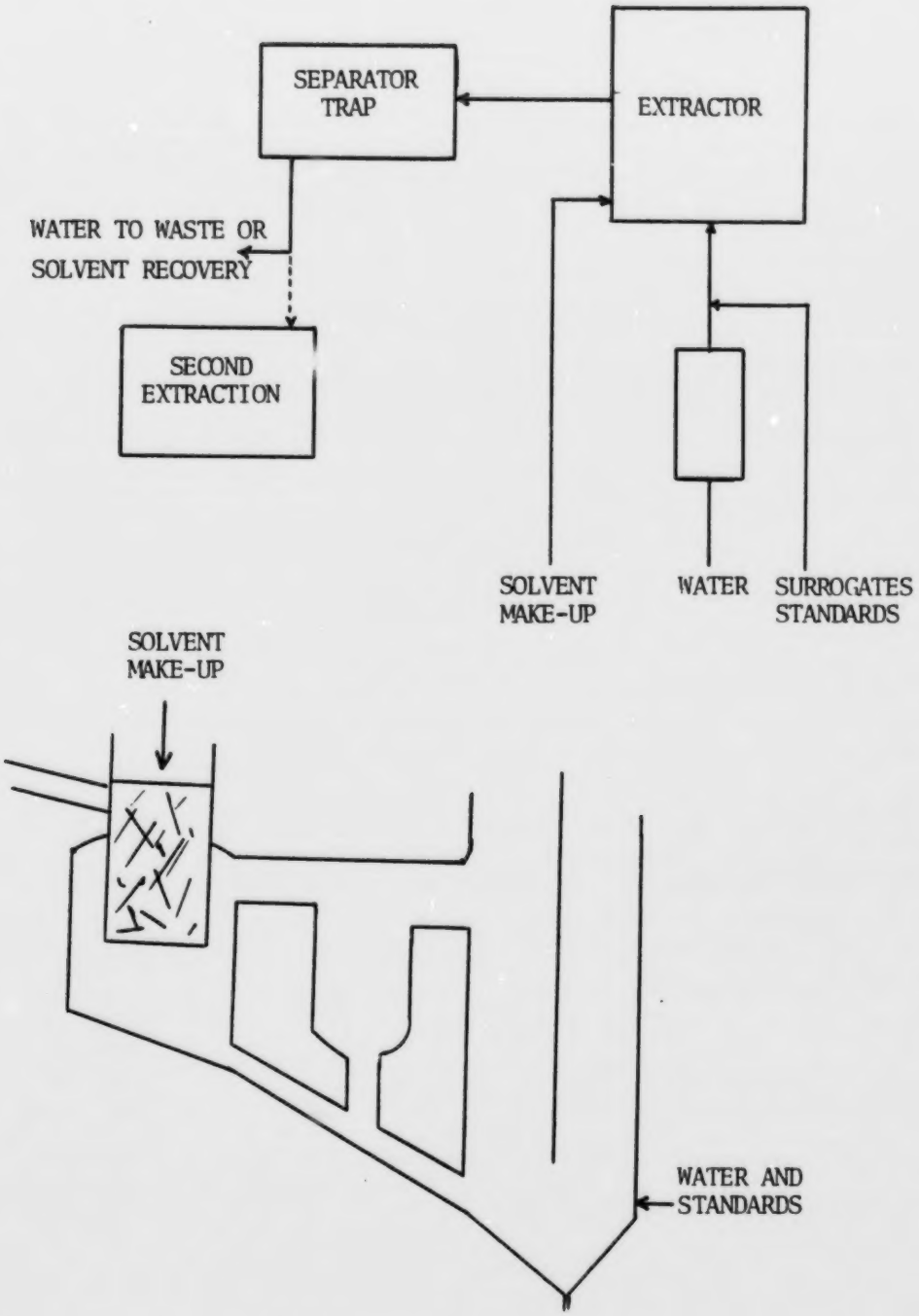


solvent is returned to the top of the column. Recovery studies with synthetic and spiked samples have shown that essentially complete extraction is obtained in this equipment.

To study the recovery, surrogate standards* are metered into the water sample as it enters the extractor. For each sample analyzed the recoveries of these surrogate standards are determined and a material balance obtained. Up to five surrogate standard materials can be used. Many hundreds of samples have been processed, each one giving measures of recovery. Further validation of the extraction efficiency was obtained by carrying out a second extraction on the water living the extractor. This allows the extraction efficiencies for both the materials present in the water sample and the surrogate standards to be determined. This second extraction has been carried out on a limited number of samples.

The first operating models of the liquid-liquid extractor were used in the Water Quality National Laboratory (WQNL) in early 1985. The extractors were first used in the field aboard the CSS Limnos in the September 1985 cruise. They have been used also in the 1986 and 1987 cruises on the Great Lakes. They were "batch" extractors, which extract water at flow rates of up to 1 L per minute.

*Solutions with known concentrations of compounds not known to exist environment but which are chemically similar to environmental contaminants. Examples of surrogate compounds are various dibromobenzenes, chemically similar to chlorobenzenes known environmental contaminants.



LIQUID - LIQUID EXTRACTOR

For monitoring the Niagara River, the extractors were modified to extract water at 35 mL per minute, for 24 hours (to give a 50 L sample). These have been in operation at the WQB station at Fort Erie and Niagara-on-the-Lake since April 1986.

A prototype sampler that takes a week-long integrated sample totaling 100 L was built and operated at Niagara-on-the-Lake for an eight month period (May to December 1986). This is an automated system for unattended operation: each day it empties and collects the solvent extract and replaces it with fresh solvent. Thus the system handles the possible variations in the concentration of organic compounds over the week.

One area of concern with the extractor, as first developed, was that it was open to the atmosphere at some points, thus giving the possibility of operator exposure to DCM vapours and of contamination of the solvent extract by the atmosphere. Versions of the extractor that are enclosed have since been developed and it is planned to use an enclosed extractor at the Niagara River monitoring station. Another concern was that the water leaving the extractor contained 1.5% DCM. Thus, if no solvent recovery system was used, 750 mL DCM were returned to the sampled water body for every 50 L sample taken. To avoid this it is planned to add a solvent recovery system to the two extractors used on the Niagara River.

SAMPLE PREPARATION BY CONTINUOUS LIQUID-LIQUID EXTRACTION (CLLE) FOR BROAD SPECTRUM ANALYSIS

I.H. (Mel) Suffet, Ph.D.
Environmental Studies Institute
Drexel University
Philadelphia, PA 19104

Identification and quantification of trace organic compounds in water has continued to be of great concern for the evaluation of health effects. Since the majority of trace organic constituents in natural and drinking waters, are below the 1 µg per liter level, an efficient enrichment step is necessary in any analytical scheme. Also, biological testing, such as the Ames test, requires the exposure of test species to chemicals at levels higher than those present in the water being tested, thus also implying an efficient enrichment step.

Among the most widely used techniques to isolate organic compounds from water is liquid-liquid extraction (LLE). For example, batch extraction methods with methylene chloride are used for specific groups of EPA Priority Pollutants (Methods 602-610, U.S. EPA, 1984). The EPA has also proposed a broad spectrum batch LLE method for concentration of acid, base and neutral compounds into methylene chloride (Method 625, U.S. EPA, 1984). These methods have usually been applied to grab samples, although composite sampling is also possible.

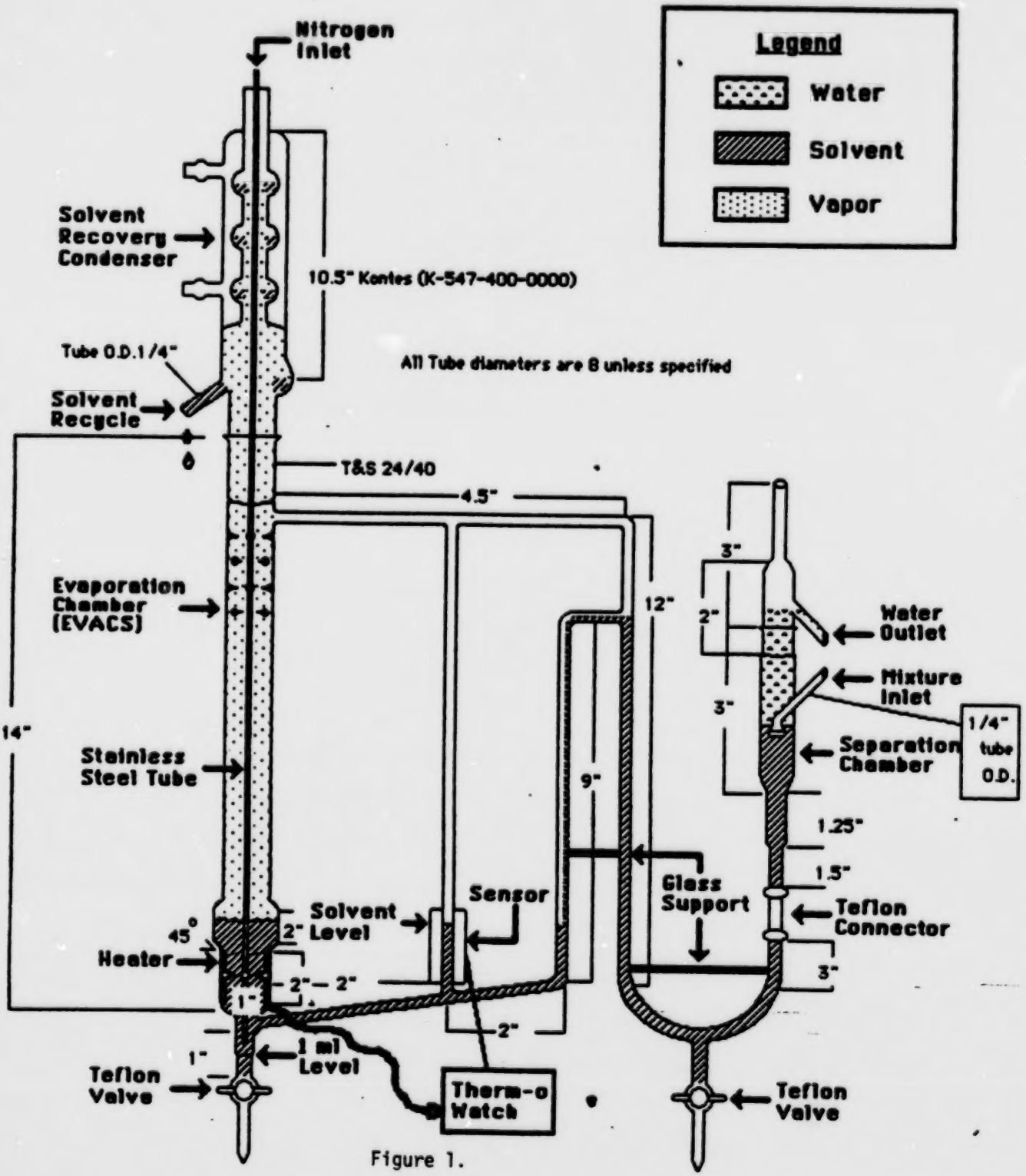

Legend
Water
Solvent
Vapor
Nitrogen Inlet
Solvent Recovery Condenser
10.5" Kontes (K-547-400-0000)
Tube O.D.1/4"
All Tube diameters are 8 unless specified
Solvent Recycle
T&S 24/40
4.5"
Evaporation Chamber (EVACS)
12"
3"
2"
Water Outlet
Mixture Inlet
3"
1/4" tube O.D.
Separation Chamber
14"
Stainless Steel Tube
9"
1.25"
1.5"
Glass Support
Teflon Connector
Sensor
Solvent Level
45°
2"
Heater
2"— 2"
1"
3"
2"
1"
1 ml Level
Teflon Valve
Therm-o Watch
Teflon Valve

Figure 1.

An on-line continuous liquid-liquid extraction (CLLE) system using a teflon coil has been developed in our laboratories, and has been tested on the isolation of ng per liter concentrations of organophosphate pesticides from samples of fortified natural waters (Wu and Suffet, 1975 and 1977), and of a broad spectrum of gas chromatographable trace organics present in drinking water by on-line composite sampling (Yohe et al., 1985).

Recently, the teflon helix CLLE was modified to improve its efficiency and reliability and to determine the efficiency of the extractor with methylene chloride (Figure 1) (Baker et al., 1987; Baker and Suffet, 1987). Methylene chloride is the solvent of choice for EPA priority pollutant analysis (U.S. EPA, 1984) and the EPA Master Analytical Scheme (Pellazzari et al., 1984). The newer version of the teflon helix CLLE has also been used to isolate and concentrate chemicals for the Ames Mutagenicity Test (Lippincott et al., 1987).

Recovery and reproducibility were the criteria used to evaluate performance of the newest version of the extractor at µg per liter concentrations (Baker et al., 1987). Solutions containing up to 13 non-polar organic compounds were added to deionized, organic free (Milli-Q) water containing a salt matrix. The salt concentrations were similar to what might be found in a surface water high in total dissolved solids, or in a typical surface water sample concentrated by reverse osmosis. This solution was extracted under controlled conditions by

batch and continuous extraction at a 10 to 1 water to solvent ratio. Recoveries were determined at higher concentrations (µg per liter range) so that direct analysis of the extract was possible without solvent evaporation. Thus, actual CLLE and batch LLE recoveries could be compared to the theoretical optimum recoveries defined by partition coefficients. CLLE recoveries were determined at pH 3 and 7. The comparison at pH 3 was made with and without a humic substance present.

An experimental design was developed to enable the CLLE recoveries be compared to:

(1) those theoretically possible as defined by the partition coefficients of the test compounds,

(2) batch extraction recoveries using the smae aqueous solutions under the same conditions, and

(3) those from different size samples.

An additive error model was developed to define the precision of CLLE recovery and to determine whether or not CLLE operation contributes significantly to total error in the sampling-analysis system.

The results of this study showed that CLLE and batch LLE recoveries are statistically equivalent for most compounds, under the conditions tested, and that the presence of the humic material has similar effects on CLLE and batch LLE (Figure 2). CLLE sampling was found to be reproducible and therefore suitable for extracting nonpolar organics from water samples for use in biological testing. The CLLE reliably sampled a series of 100 liter samples of drinking water in the field, in an on-line and continuous mode, during studies at seven water treatment plants (Lippincott et al., 1987).

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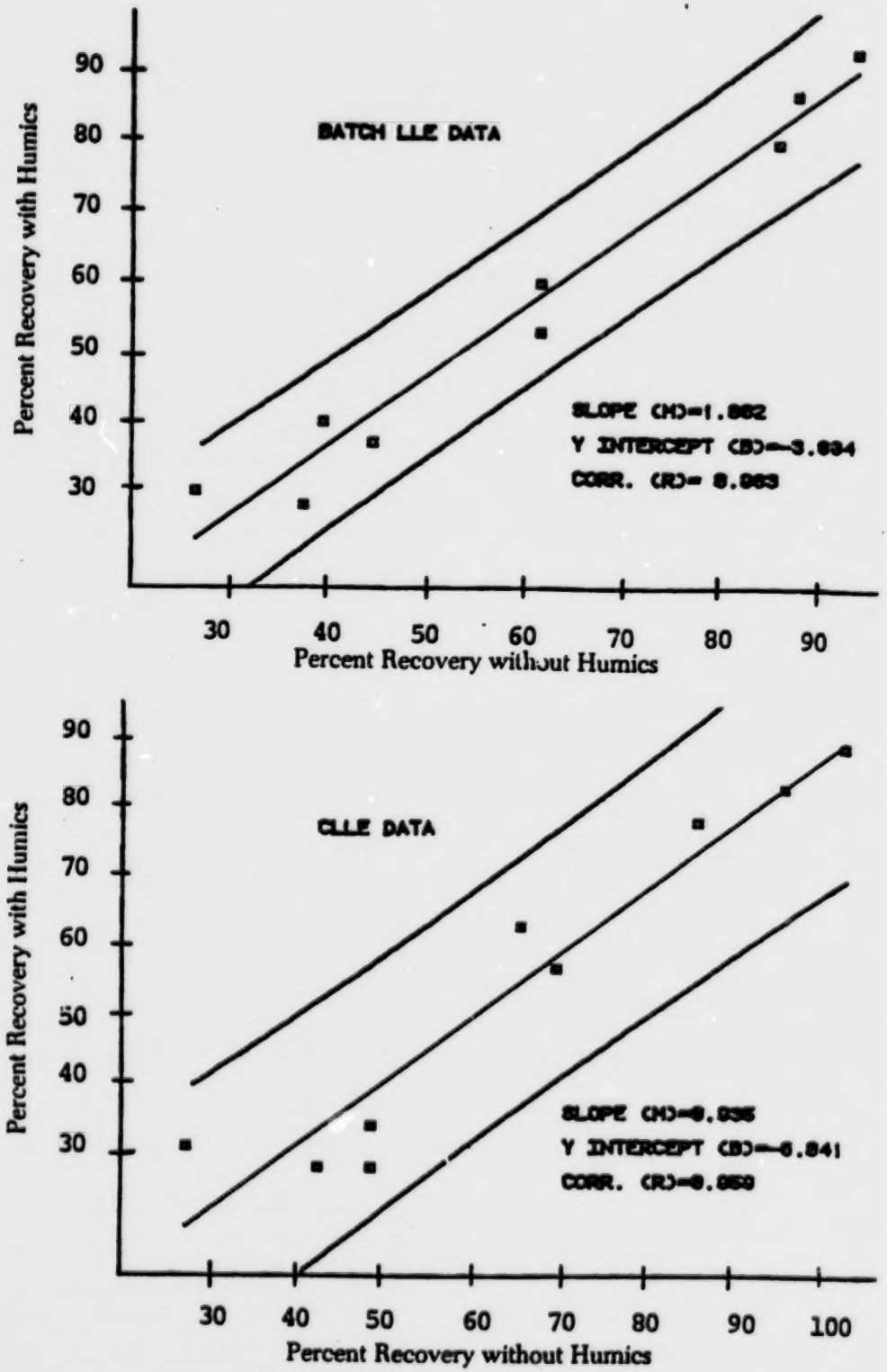

Figure 2. Linear regressions of humic versus nonhumic recovery data for 1-L batch versus 1-L continuous liquid-liquid extractions.

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ANALYSIS OF DRINKING WATER - EXPERIENCE ON USE OF XAD-2 RESIN

Guy L. Lebel
Monitoring & Criteria Div., Environ. Health Dir.
Health & Welfare Canada, Tunney's Pasture
Ottawa, Ont. K1A 0L2

Because of Health and Welfare Canada involvement in evaluating health safety and setting guidelines for drinking water quality, there is a need to analyze drinking water for the presence of organic residues. The organic level can vary widely ranging from mg/L (TOC), ug/L (THM's) to ng-pg/L (OC's, PAH's). Also, some of the compounds may be present in the water sources (humic substances), introduced by the treatment process (THM's) or may be leached from the distribution system (i.e., tributoxyethyl phosphate from tap seals/o-rings).

In an effort to devise a screening method to concentrate/isolate a wide range of organic classes for analysis by a single method (GC/MS-full scan), a sampling cartridge using Amberlite XAD-2 has been developed (1). It isolates "non-polar" organics from large volume of water (200 L). This allows enough analyte in the extract to attain ca.1 ng/L detection limits by GC/MS-full scan. Better detection limits can be obtained by using specific detectors although clean-up stages may be required (4,7). Over the past 10 years, the method has been validated for organochlorine pesticides (2), contaminants (3), PCB's (4),

organophosphate pesticides (1), triaryl/alkyl phosphates (5), polyaromatic hydrocarbons (6) and dioxins/furans (7). The extracts have been also used for testing for biological activity (Ames test) (8).

Some factors that were considered in using the adsorbent technique were:

- resin type - several resins are available for various type of organic compounds. In this case Amberlite XAD-2 was chosen and applied to "non-polar" groups of organics.

- resin purity - Soxhlet extraction with a sequence of solvents is usually applied to clean the resin. The method is time consuming. In this application ultrasound was used for clean up of the resin and it was found adequate for the groups of organic compounds evaluated.

- sampling rate - 3 bed-volume/min always used.

- cartridge size - a 20:1 length to id ratio was used for the standard cartridge and a 10:1 for the enlarged cartridge (ref. 3).

- sampling method - no difficulties were encountered when sampling from a pressurized tap. When sampling by gravity feed, however, air pockets from dissolved gases were formed in the resin bed causing considerable flow reduction.

- stripping solvent - a mixture of 15% acetone in hexane was used and found to be adequate for all compounds tested as well as all mutagens.

- spiking technique - continuous fortification using a pump to feed a "concentrated" aqueous solution was found to be preferable to the direct spiking technique used earlier. Adsorption problems were encountered when pumping dioxins from aqueous solution at low flows using teflon lines. Methanol spiking solution can be used but the addition of this alchool to the water stream may affect adsorption. In this work, the amount of methanol (0.1-0.5%) did not influence dioxins adsorption (unpublished results).

- other factors such as production of blanks (very difficult to obtain "large" volume of purified water), regeneration of resin, and filtering of sample.

The XAD scheme has been used in several surveys for various classes of organics. Results reveal widespread presence of some triaryl/alkyl phosphates, some regular and oxygenated PAH's and also alpha-BHC. Biological assays (Ames test) of the extracts show mutagenic activity on treated water but rarely on raw water.

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PRECONCENTRATION OF TRACE ORGANIC COMPOUNDS FROM LARGE VOLUMES OF WATER.

R.E. Clement, S.A. Suter and H.M. Tosine

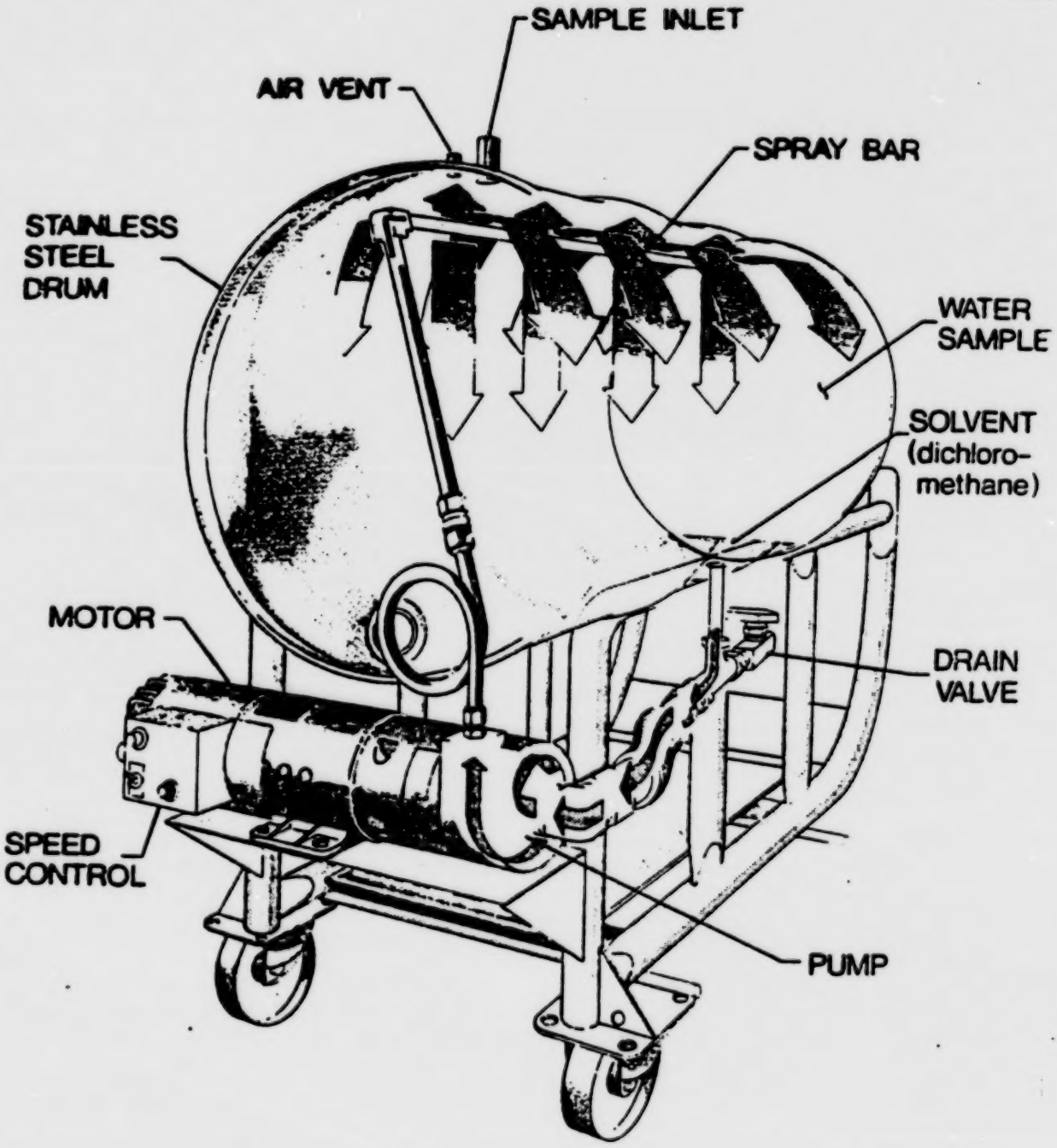
Ontario Ministry of the Environment, Laboratory Services Branch
P.O. Box 213, (125 Resources Road), Rexdale, Ontario M9W 5L1

The Aqueous Phase Liquid Extractor (APLE) is a device capable of extracting up to 200 L of water in a single batch process. It is essentially a large drum with a spray-bar across the top, and a pump to recirculate heavier-than-water solvent to the spray bar. Excellent contact between the water and solvent during the recirculation process allows a 200 L water sample to be extracted rapidly and on-site. Water must be particulate-free to avoid clogging of the spray-bar, therefore samples are centrifuged before extraction. Particulate samples and solvent extracts were returned to the laboratory for further processing.

Sampling was performed on two separate days at Pettit Flume on the upper Niagara River. This location was chosen because previous analysis of common shiners from this area exhibited high ppt levels of CDD/CDF congeners, including 2,3,7,8-TCDD. Pettit Flume is a discharge point of a storm sewer and small stream which includes the Occidental/Durez facility storm water discharge in North Tanawanda, New York. A natural source of CDD/CDF in water is desirable for method development studies of water extraction methods, because of the difficulties in performing spiking studies using hydrophobic analytes. During the first sampling period, continuous precipitation was experienced , while a discharge pipe flowed continuously. The second day, there was no precipitation and only a small trickle flowed from the discharge pipe. Conventional 10 L water samples were also taken, to compare results from APLE extraction to standard liquid/liquid extraction.

A large variation in CDD/CDF results on different days was observed. Much greater concentrations were detected in samples taken during heavy flow of the discharge pipe. Because of the developmental nature of this work, these data cannot be used to determine the total environmental input of CDD/CDF from this location.

In this presentation, comparisons of the use of the APLE versus standard liquid/liquid extraction, and the particulate/aqueous distributions of CDD/CDF, will be presented. Spiking studies, analytical methodology and the problems and benefits of the APLE will be discussed. Complete sampling data for CDD/CDF from the Pettit Flume location will be presented.



APLE (AQUEOUS PHASE LIQUID EXTRACTOR)

Developed by IMC, CCIW.

Built for the Ministry by Zenon Environ.

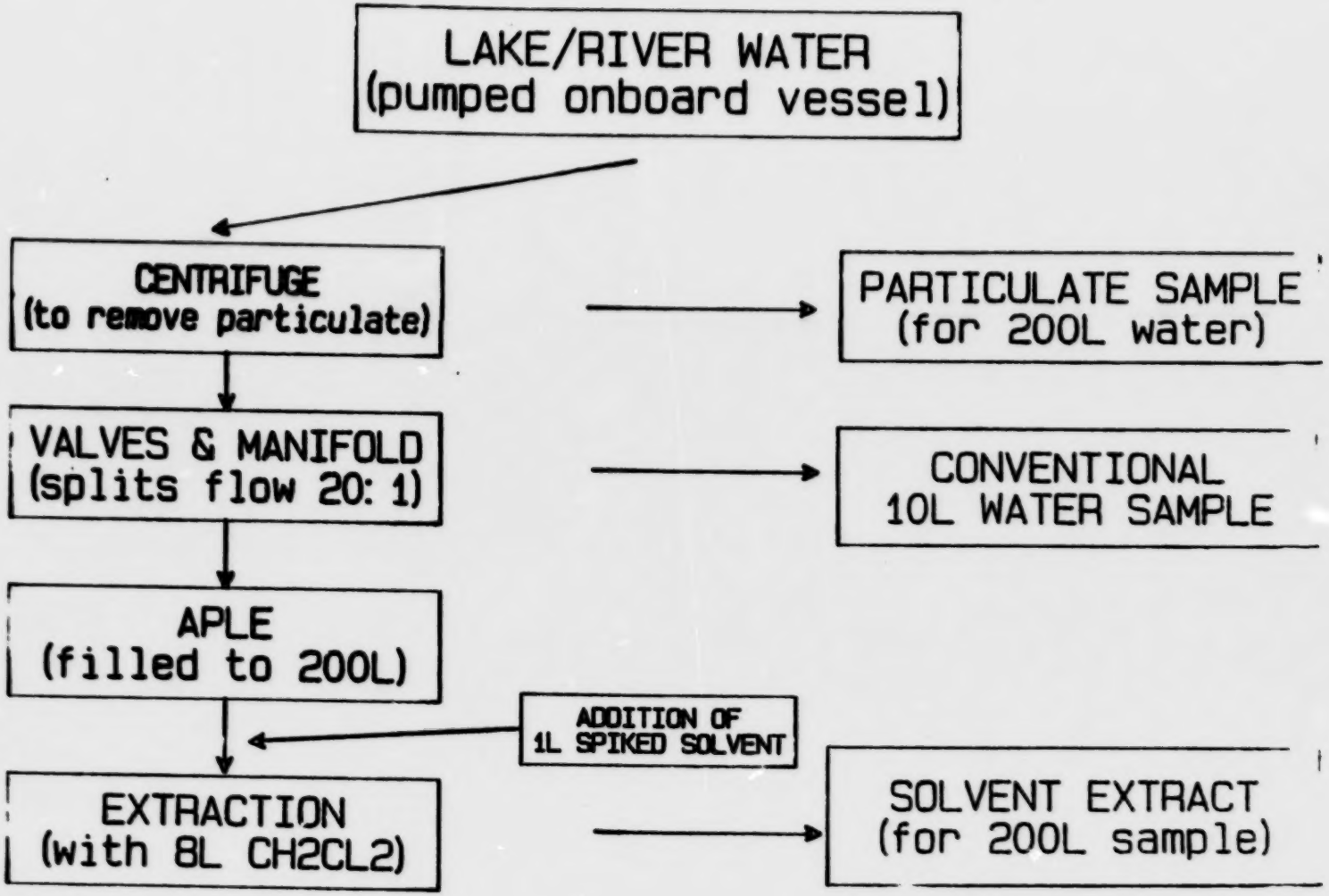
NOVEMBER 5, 1985

CONTINUOUS RAINFALL ALL DAY
WITH LIGHT FOG
DISCHARGE PIPE INTO INLET FLOWED
CONSTANTLY ALL DAY

NOVEMBER 6, 1985

LIGHT MIST ALL DAY WITH NO
HEAVY RAINFALL
SLIGHT TRICKLE FROM DISCHARGE PIPE

SAMPLING EVENT



APLE SOLVENT SAMPLE - 200L WATER

DECANT
(to remove water)

↓

ADD ANALYTICAL SPIKE
(13C-TCDF)

↓

ROTARY EVAPORATION
(concentrate the extract)

↓

DUAL-COLUMN CLEANUP
(modified DOW)

CONCENTRATION
(under N2 to 25 mls)

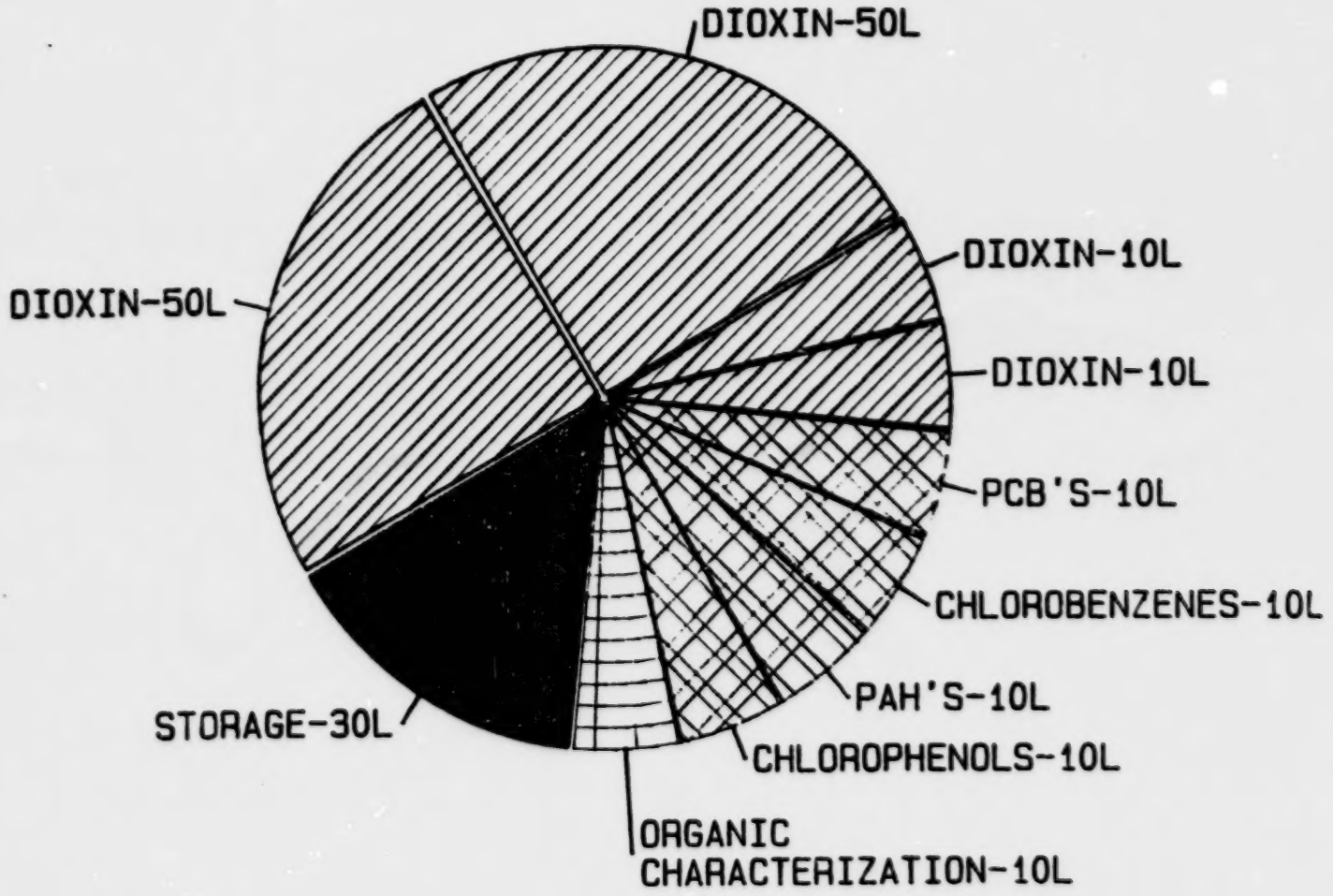
↓

TRANSFER
(to 250ml v.flask)

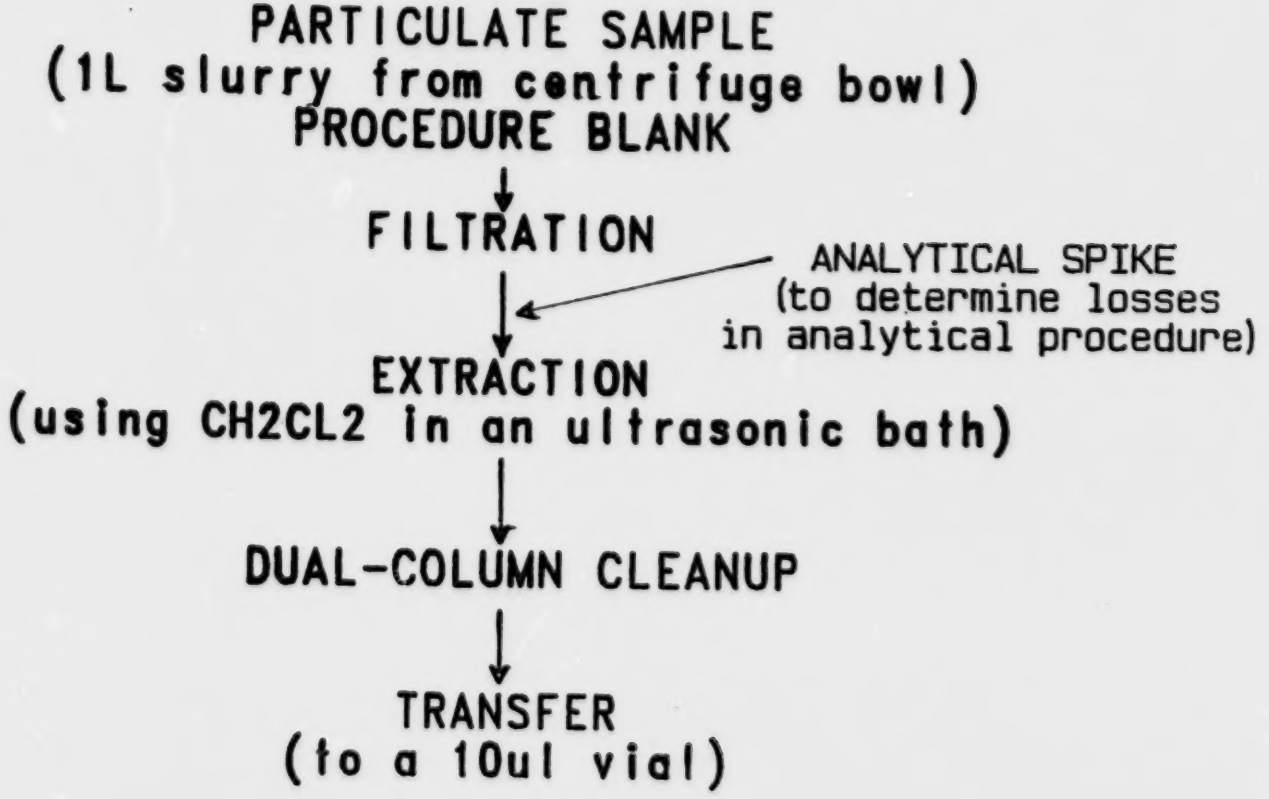
↓

SAMPLES SPLIT

200 LITRE APLE
SPLIT ANALYSIS SCHEME



PARTICULATE METHODOLOGY



SUBMIT FOR GC/MS ANALYSIS

CONVENTIONAL WATER METHOD

10 L WATER SAMPLE
(from manifold)

ANALYTICAL SPIKE
(to determine losses
in analytical procedure)

↓

LIQUID/LIQUID EXTRACTION
(1L aliquots with pentane)

↓

DUAL-COLUMN CLEANUP
(modified DOW method)

↓

CONCENTRATION
(under N2)

↓

TRANSFER TO 10uL VIAL AND
SUBMIT TO GC/MS

SAMPLE TYPE	SPIKE LEVELS 13CTD	13CTF	13COD	RECOVERIES 13CTD	13CTF	13COD
APLE #1&2 - 10L CONVENTIONAL	1NG		1NG	140		65
				31		55
APLE #1&2 - 50L SOLVENT A	*5NG	5NG	*5NG	*51	120	*60
				*25	64	*28
APLE #1&2 - 50L SOLVENT B	*5NG	5NG	*5NG	*53	86	*100
				*28	93	*39
APLE #1&2 - 10L SOLVENT A	*1NG	1NG	*1NG	*62	95	*98
				*28	95	*25
APLE #1&2 - 10L SOLVENT B	*1NG	1NG	*1NG	*73	95	*100
				-	-	-
APLE #1&2 - PARTICULATE	10NG		20NG	110		97
				99		72

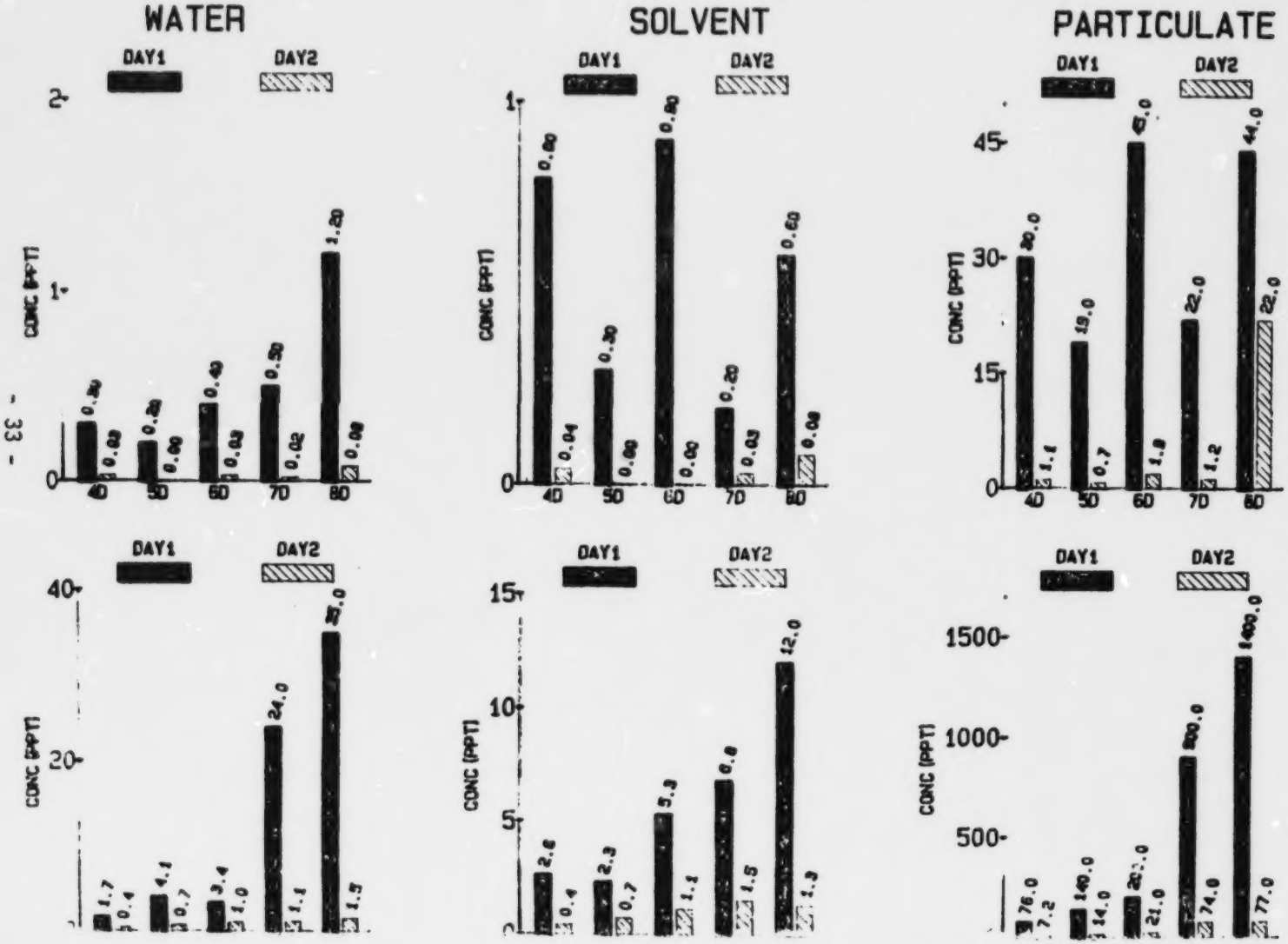
*FIELD SPIKE, USED TO DETERMINE THE RECOVERY FROM APLE EXTRACTION
ANALYTICAL SPIKE, USED TO DETERMINE LOSSES DUE TO SAMPLE PREP.

DIOXIN/FURAN DATA - PETIT-FLUME

DIOXINS/ FURANS	DAY1 APLE 10L CONV.H2O	DAY1 APLE 50L SOLVENT	DAY1 APLE SLURRY	DAY2 APLE 10L CONV.H2O	DAY2 APLE 50L SOLVENT	DAY2 APLE SLURRY
T4CDD	0.3 (3)	0.8 (2)	30 (4)	0.03 (4)	0.04 (2)	1.1 (4)
P5CDD	0.2 (4)	0.3 (1)	19 (5)	ND	ND	0.7 (5)
H6CDD	0.4 (5)	0.9 (3)	45 (5)	0.03 (4)	ND	1.9 (5)
H7CDD	0.5 (2)	0.2 (2)	22 (2)	0.02 (2)	0.03 (1)	1.2 (2)
O8CDD	1.2	0.6	44	0.08	0.1	22
TOTAL DX:	**2.6**	**2.8**	**160**	**0.16**	**0.17**	**26.9**
T4CDF	1.7 (10)	2.6 (6)	76 (10)	0.4 (9)	0.4 (5)	7.2 (11)
P5CDF	4.1 (10)	2.3 (3)	140 (7)	0.7 (9)	0.7 (8)	14 (8)
H6CDF	3.4 (4)	5.3 (6)	200 (5)	1.0 (4)	1.1 (9)	21 (7)
H7CDF	24 (3)	6.8 (3)	900 (4)	1.1 (3)	1.5 (4)	74 (3)
O8CDF	35	12	1400	1.5	1.3	77
TOTAL FN:	**68.2**	**29**	**2716**	**4.7**	**5.0**	**193.2**

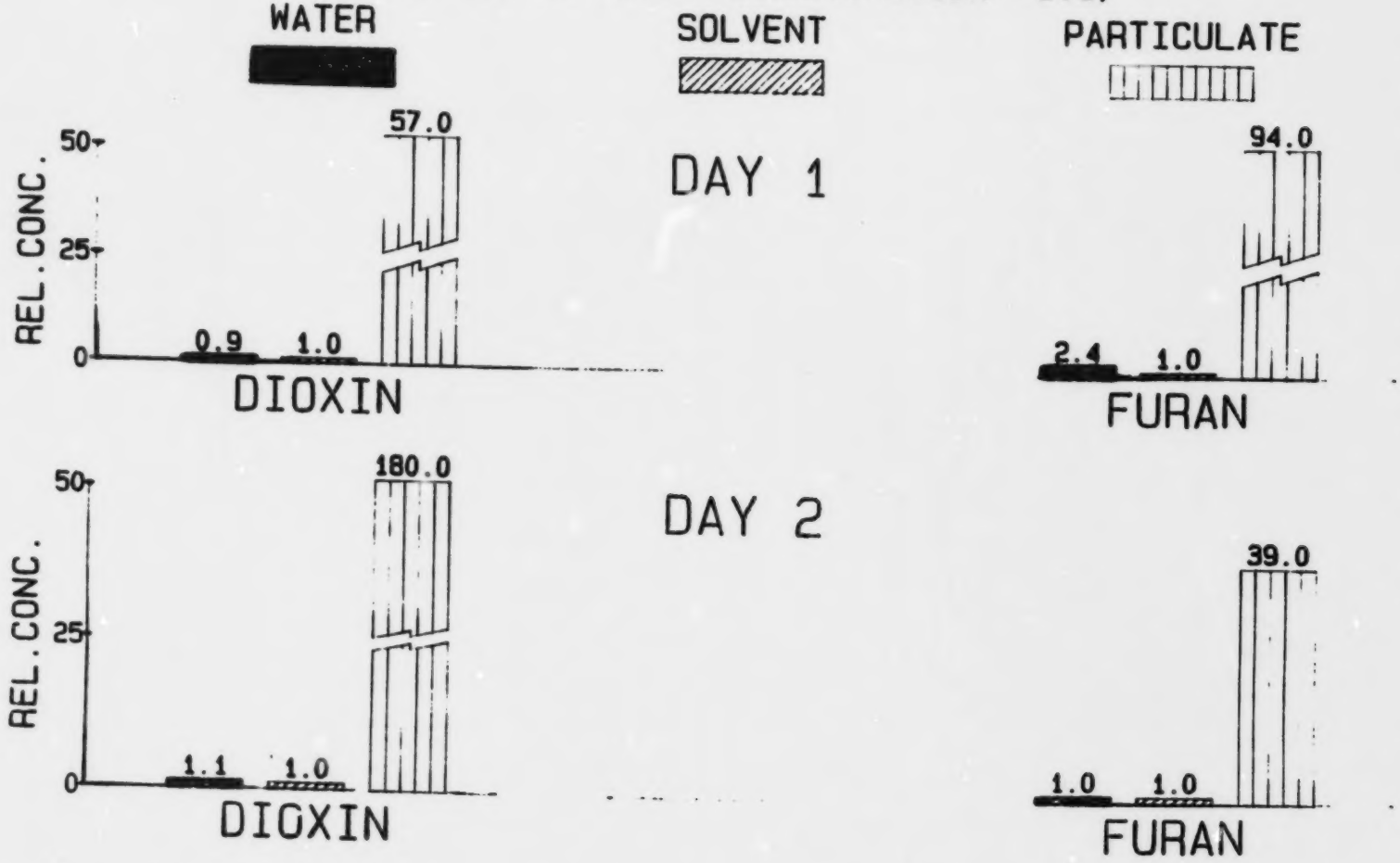
ALL DATA EXPRESSED IN PARTS PER TRILLION (PPT), CORRECTED FOR INT. SPIKE RECOVERIES, ND=NOT DETECTED, ISOMERS ARE SHOWN IN BRACKETS

DIOXIN/FURAN CONGENER DISTRIBUTION



RELATIVE CDD/CDF CONCENTRATIONS IN THE CONVENTIONAL WATER AND THE APLE SAMPLES

(normalized to APLE concentration =1.0)



CONCLUSIONS

THESE DATA INDICATE THAT LITTLE DIFFERENCE EXISTS BETWEEN THE LEVELS OF CDD/CDF'S FOUND USING THE APLE SAMPLER VERSUS THE CONVENTIONAL 10 LITRE SAMPLING SCHEME

FURAN CONGENERS WERE ALWAYS PRESENT IN CONCENTRATIONS GREATER THAN THAT OF DIOXIN CONGENERS

THE CONCENTRATIONS OF DIOXINS/ FURANS ARE CONSIDERABLY GREATER ON THE SUSPENDED PARTICULATE AS COMPARED TO THE CONCENTRATIONS FOUND IN THE AQUEOUS PORTION

THE APLE SAMPLER IS TOO BULKY AND CUMBERSOME TO SUIT THE NEEDS OF MOE AS A PORTABLE SAMPLING SYSTEM FOR DRINKING WATER, BUT COULD BE USED FURTHER IN VARIOUS SURFACE WATER STUDIES

EXTRACTION OF TRACE ORGANICS WITH AMBERLITE XAD-7 AND SEPHADEX QAE

Gordon Kan, Ph. D.
Water Quality Branch
Pacific & Yukon Region

Abstract: A new sampler employing a mixture of XAD-7 and Sephadex A-25 as absorbents to concentrate trace organics from 50 L of river water in 4-6 hrs was developed. Trace organic compounds concentrated on the resins were desorbed with acetone and methylene chloride and segregated into two major classes: base-neutral and acid-extractables. Spike-recovery studies with representative compounds chosen from organochlorides, organophosphates, PCBs, chlorophenols and herbicides, and comparative studies with liquid/liquid extractor were conducted. Our understanding of the resins and the advantages/disadvantages of the samplers will be discussed.

The purpose of my talk is to describe to you the water sampler that we have developed, using a mixture of resins, XAD-7 and Sephadex QAE A-25. The development of this sampler was based on the ideas and information that had been published in the following literature:

Slide 1

References

1. S.F.Stepan, et.al., Water Research, 11, 339(1977).

-extraction efficiency of phenol was enhanced by XAD-7 over XAD-2.
-extraction efficiency of organic acids was significantly increased under acidic conditions.

2. S.F.Stepan, et.al., Water Research, 12, 447(1978).

-apparatus for on-site extraction of organics from water.

3. Lars Renberg, Anal.Chem.,46,458(1974).

-use of Sephadex QAE A-25 for determination of chlorinated phenols and phenoxy acids in tissue, soil, and water.

4. M.Goto, et.al., Environ.Sci & Technol., 20, 463(1986).

-adsorption of phenol on anion exchange resin and activated carbon.
-phenol may be desorbed by both acid or base from anion exchange resin.

5. S.Goto, et.al., J.Chem.Eng.Japan, 17,204(1984).

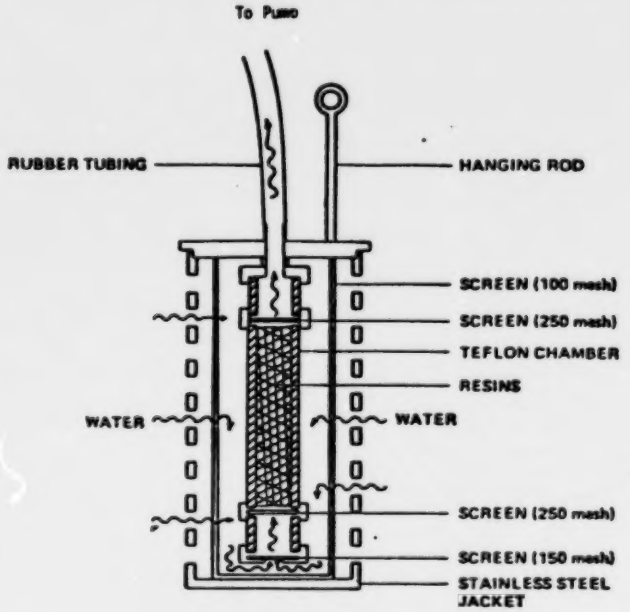
-in aqueous solution, phenol adsorption was due to physical interaction besides ion exchange mechanism.

6. R.Pocklington, Marine Chem., 13, 255(1983).

-no significant advantage of XAD-8 over XAD-2 for extraction of organic matter from seawater.
-efficiencies of up to 90% were obtained when seawater was acidified.

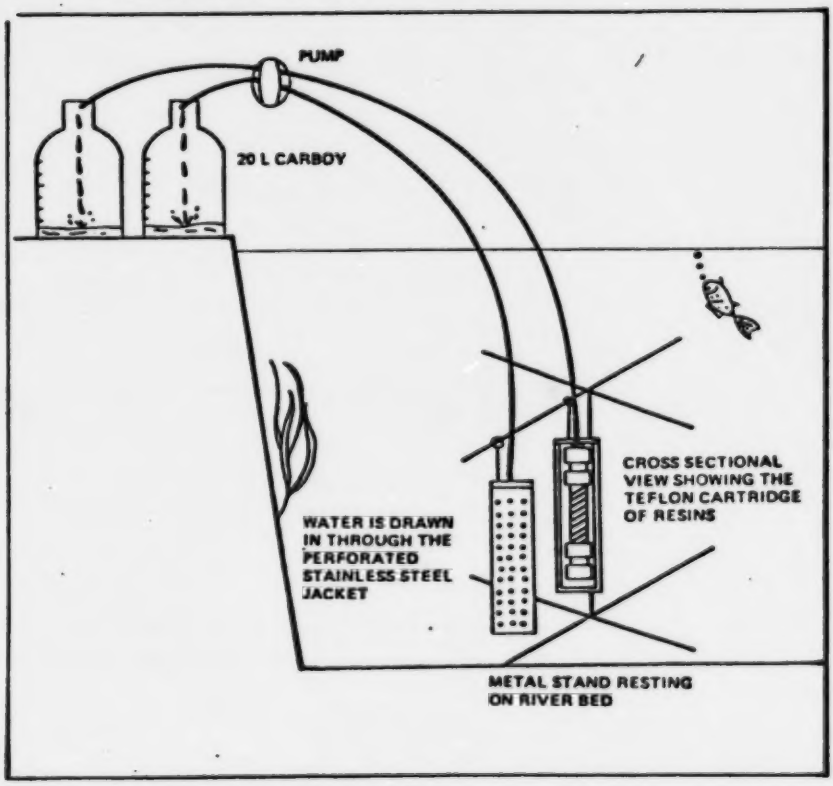
Let us take a look at the sampler that we have designed (Slide 2). During operation, a pair of samplers might be attached to a metal stand to be lowered into the river. A peristaltic pump with dual pump heads might be used to draw water through the resins cartridges (Slide 3)

Slide 2



Cross-sectional view of Organic Sampler.

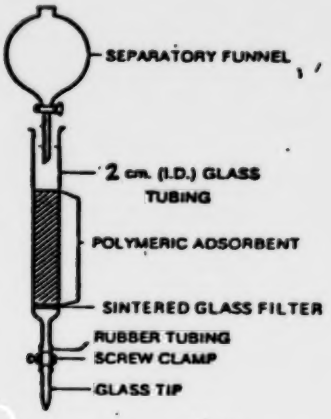
Slide 3


PUMP
20 L CARBOY
CROSS SECTIONAL VIEW SHOWING THE TEFLON CARTRIDGE OF RESINS
WATER IS DRAWN IN THROUGH THE PERFORATED STAINLESS STEEL JACKET
METAL STAND RESTING ON RIVER BED

Organic Sampler in Action.

At the end of the run, the resins were transferred to a LC column (Slide 4) and the resins were desorbed in the following manner (Slide 5).

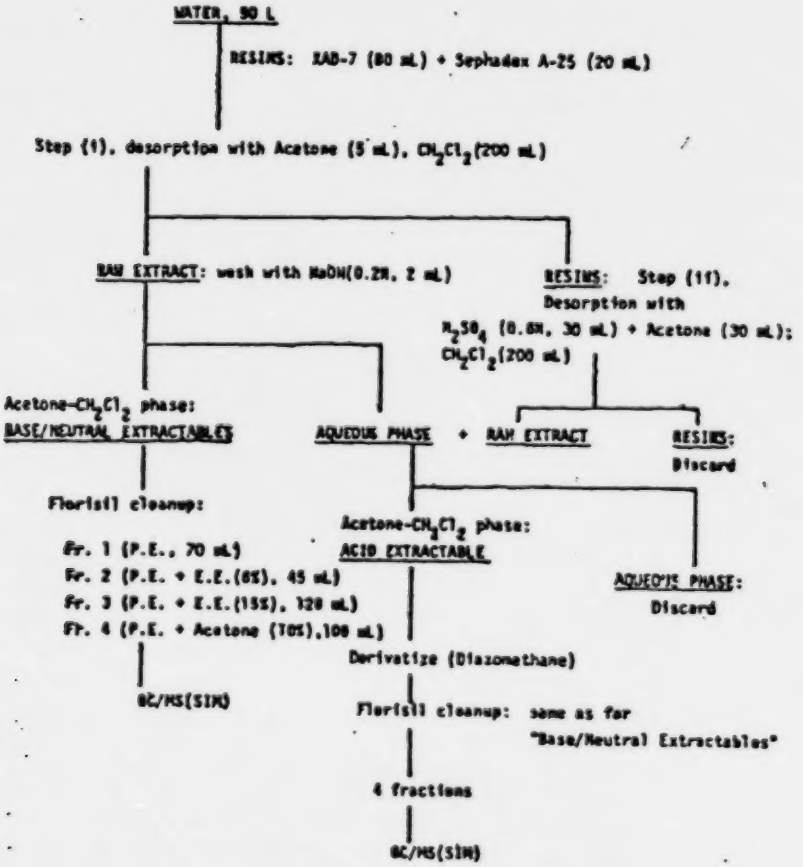
Slide 4



Illustrative Liquid Column Chromatography.

Slide 5

SCHEME 1. Analysis scheme for separating raw sample extract into Base/Neutral and Acid Extractable organics.


WATER, 90 L
RESINS: XAD-7 (80 mL) + Sephadex A-25 (20 mL)
Step (i). desorption with Acetone (5 mL), CH_2Cl_2 (200 mL)
RAW EXTRACT: wash with NaOH(0.2N, 2 mL)
RESINS: Step (ii). Desorption with H_2SO_4 (0.6N, 30 mL) + Acetone (30 mL); CH_2Cl_2 (200 mL)
Acetone-CH_2Cl_2 phase: BASE/NEUTRAL EXTRACTABLES
AQUEOUS PHASE + RAW EXTRACT
RESINS: Discard
Florisil cleanup:
Fr. 1 (P.E., 70 mL)
Fr. 2 (P.E. + E.E.(6%), 45 mL)
Fr. 3 (P.E. + E.E.(15%), 120 mL)
Fr. 4 (P.E. + Acetone (70%), 100 mL)
GC/MS(SIM)
Acetone-CH_2Cl_2 phase: ACID EXTRACTABLE
AQUEOUS PHASE: Discard
Derivatize (Diazomethane)
Florisil cleanup: same as for "Base/Neutral Extractables"
4 fractions
GC/MS(SIM)

Before I show you the results that we have obtained by this sampler I would like to share with you our knowledge and understanding of the resins:

Slide 6

Amberlite XAD's are synthetic cross linked polymers. Some of the properties of XAD resins are summarized below:

Resins	Chemical Nature	Porosity Volume, %	True Wet Density g/cc	Surface Area m^2/g	Avg. Pore Diameter Angstroms
XAD-1	Polystyrene	37	1.02	100	200
XAD-2	Polystyrene	42	1.02	330	90
XAD-4	Polystyrene	51	1.02	780	50
XAD-7	Acrylic ester	55	1.05	450	80
XAD-8	Acrylic ester	52	1.09	140	250

Amerlite XAD-7 is not to be confused with ion exchange resins since it contains no ionically functional groups attached to the resin structure. In the absence of functional sites, the polymeric adsorbent derives its adsorptive properties from its macroreticular porosity, high surface area and the aliphatic nature of its structure.

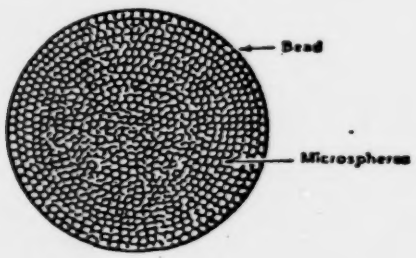
Characteristic Properties of XAD-7:

Appearance.....opaque, 20-50 mesh beads.
Average particle diameter.....0.3 to 0.45 mm
Wet density, in distilled water.....1.05 g/ml
Porosity of beads.....0.5 to 0.55 ml of pore/ml bead
Surface area.....450 square m/g
Average pore diameter.....80 Angstrom units

Slide 7

MACRORETICULAR STRUCTURE OF XAD-7:

To better understand the phenomena through which Amberlite XAD-7 functions, it is helpful to consider the individual beads each to be an agglomerate of a large number of very small microspheres as shown on the sketch below.



The macroreticular structure results in a continuous solid phase as well as a continuous pore phase. The pores will be filled with solvent during use, thereby exposing a large surface area of the resin to the solvent and solute molecules. This results in rapid diffusion of solvent and solute around the microspheres, and hence a fast flow rate should be avoided during columnar operation.

Slide 8

DRIVING FORCE IN PHYSICAL ADSORPTION:

The dissolution of organic molecules in water is accompanied by a negative entropy change, resulting from orientation of water molecules around the organic species. As organic molecules are adsorbed onto the surface of the adsorbent, the oriented water molecules are released, with the accompanying entropy increase. This entropy gain is the principal driving force in physical adsorption of organic molecules from the aqueous system.

ADSORPTION FROM POLAR SOLVENTS (e.g. Water):

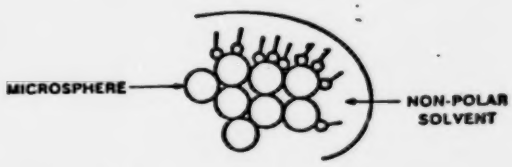
In adsorption of organic molecules from aqueous solvent, the hydrophilic and hydrophobic portions of the solute are both adsorbed onto the Amberlite XAD-7. This may be presented schematically in the sketch below which represents a greatly magnified cross-section of a portion of a bead. The solute molecule, o— , is shown as having a relatively hydrophobic portion, — , and a relatively hydrophilic portion, o.

In this case there is both polar bonding (e.g. hydrogen bonding) between the hydrophilic portion of the sorbate molecule and the aliphatic surface of the bead, as well as the normal van der Waals interaction between the hydrophobic portion and the bead.

Slide 9

ADSORPTION FROM NON-POLAR SOLVENTS:

In adsorption from non-polar solvents, that portion of the organic molecule with greater affinity for water, i.e., the hydrophilic portion, is preferentially adsorbed onto the polar surface of the resin, while the remaining portion of the molecule remains in the solvent phase which fills the pores in the bead. This may be presented schematically in the sketch below:



The exact mechanism of adsportion in any given system will depend upon the hydrophilic/hydrophobic balance of the solute and the polarity of the solvent. Since one may not always be able to predict the exact mechanism of adsorption, pilot laboratory studies are necessary.

Now, let us take a look at Sephadex which was used as an absorbent in our case.

Slide 10

SEPHADEX - ion exchange resin:

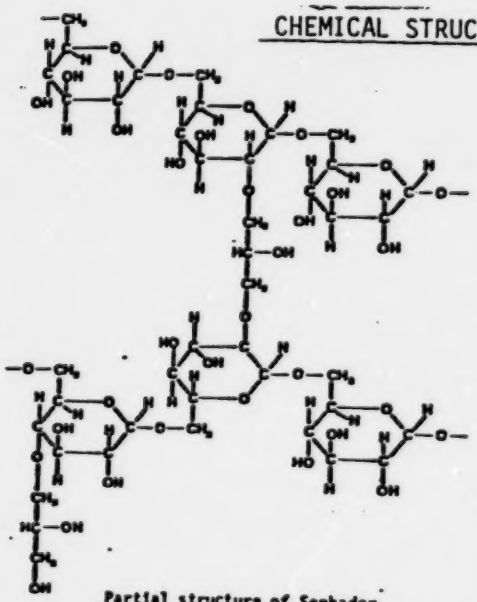
Sephadex is made of cross-linked dextran. Active ionic functional groups are attached to the glucose units by stable ether linkages. The mobile counter-ion can be exchanged with other ions of the same charge without altering the matrix.

ANION exchanger with exchangeable counter ions

CATION exchanger with exchangeable counter ions

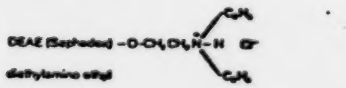
Slide 11

CHEMICAL STRUCTURE

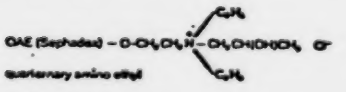


Partial structure of Sephadex.

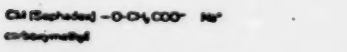
ACTIVE FUNCTIONAL GROUPS:



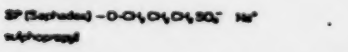
Weakly basic anion exchanger



Strongly basic anion exchanger



Weakly acdic cation exchanger



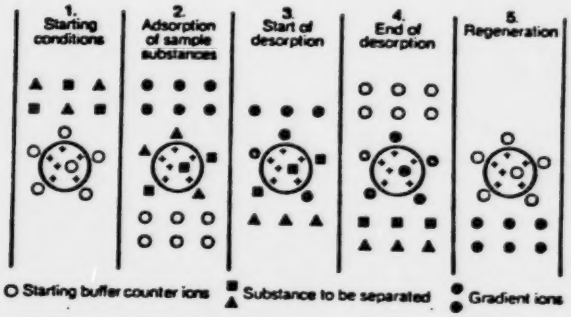
Strongly acidic cation exchanger

(The terms strong and weak refer to the extent of the variation of of ionization with pH).

Slide 12

THE THEORY OF ION EXCHANGE.

The separation of a mixture is obtained when different substances have different affinities for the ion exchanger due to differences in their charge. In addition to the ion exchange effect, other types of binding may occur. These effects are small and are mainly due to van der Waals forces and polar interactions.



Now, let me show you the results that we have obtained with our sampler that was packed with XAD-7 and Sephadex QAE. We first tried out the system in the Capilano River where the pH was about 7. The results were very satisfactory (Slide 13). We then tried it out in the Okanagan River where the pH was about 8.2; the results were very poor for pentachlorophenol and phenoxyacid herbicides (Slide 14).

Slide 13

TABLE 1. Recovery (%) of base-neutral and acid extractable organics from 20 mL of XAD-7 and 20 mL of Sephadex A-25 after allowing 50 L of natural water to pass through the resins.

Organic compounds	Amount added (ng)	Recoveries (%) (A)	(B)	(C)	Mean	St. Dev.	Coeff. Var.
PCB (1254)	500	100	100	104	101	2.3	2.3
Heptachlor	20	100	93	96	96	3.5	3.6
Aldrin	30	100	98	97	98	1.5	1.5
DDMU	100	104	100	98	100	3.5	3.0
p,p'-DDE	70	99	88	93	93	5.5	5.9
o,p'-DDT	100	101	100	97	99	2.0	2.1
Ethion	500	93	92	79	88	7.8	8.8
Lirosne	20	119	100	109	109	9.5	8.6
Heptachlor Epoxide	30	96	100	87	94	6.6	7.0
α-Chlordane	48	98	98	83	93	8.6	9.3
γ-Chlordane	40	83	94	82	86	6.6	7.7
p,p'-DDD	120	85	98	88	90	6.8	7.5
p,p'-DDT	120	100	103	85	96	9.6	10
Casoron	80	76	87	86	83	6.0	7.3
Bolfan	100	86	94	97	92	5.6	6.1
Morestan	300	93	72	75	80	11	14
2,4-D BEE	1000	98	96	93	95	2.5	2.6
α-Endosulfane	50	91	95	75	87	10	12
Dieldrin	60	103	99	85	95	9.4	9.8
Endrin	78	100	100	82	94	10	11
Methoxychlor	100	95	103	80	92	11	12
β-Endosulfane	100	80	93	64	79	14	18
Pentachlorophenol[a]	30	100+	100+	100+			
2,3,4,5-Tetrachlorophenol	50	94	79	93	88	8.3	9.4
2,4-D	300	90	39	65	71	16	23
Picloram	20	60	71	76	69	8.1	12

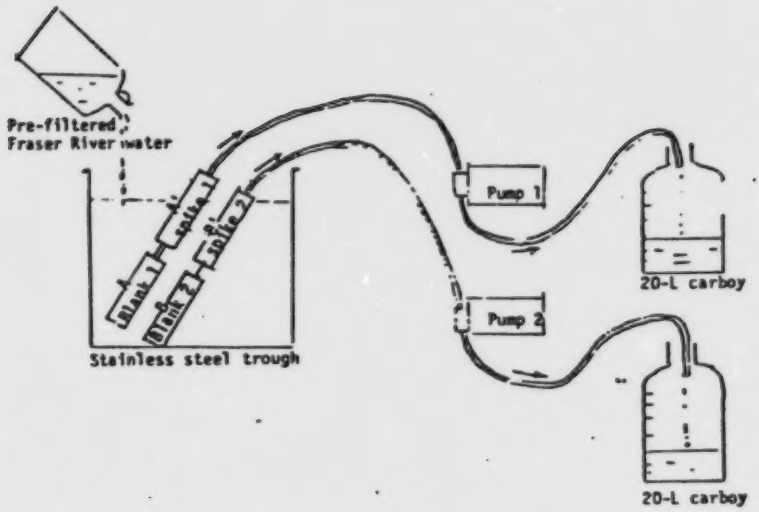
Slide 14

TABLE 2. Recovery (%) of base-neutral and acid extractable organics from 50 L of Okanagan River water at pH 8.2±0.2 .

Organic compounds	Amount added (ng)	Recoveries (%) (A)	(B)	Mean	St. Dev.	Coeff. Var.
PCB (1254)	500	96	97	96	0.7	0.7
Heptachlor	20	93	93	93	0	0
Aldrin	30	89	91	90	1.4	1.5
DDMU	100	100	98	99	1.4	1.4
p,p'-DDE	70	98	102	100	2.8	4.0
o,p'-DDT	100	92	92	92	0	0
Ethion	700	72	68	70	2.8	4.0
Lindane	20	141	135	138	4.2	3.0
Heptachlor Epoxide	80	100	100	100	0	0
α-Chlordane	40	84	94	89	7.1	7.9
γ-Chlordane	40	106	106	106	0	0
p,p'-DDD	120	110	107	109	2.1	1.9
p,p'-DDT	120	105	103	104	1.4	1.3
Casoron	80	94	93	94	0.7	0.7
Bolran	100	94	94	94	0	0
Moresian	300	72	53	63	13	21
2,4-D BEE	1000	96	86	91	7.0	7.7
α-Endosulfane	50	115	112	114	2.1	1.8
Dieldrin	60	92	92	92	0	0
Endrin	70	100	97	99	2.1	2.1
Methoxychlor	100	85	77	81	5.6	6.9
β-Endosulfane	100	95	95	95	0	0
Pentachlorophenol	120	59	20	40	27	69
2,4-D	1200	6	0	3	4.2	141
Picloram	800	0	0	0	0	0

Seeing the poor recoveries in pentachlorophenol and phenoxy herbicides, we decided to try out the system under acidic conditions. At that point in time, our priority had shifted from the Okanagan River to the Fraser River, and that our concerns were mostly on chlorophenols rather than on other pesticides. We took some Fraser River water, filtered it through glass fibre filters (GF/C) and acidified it to pH 2-3, then poured it into a clean container from which two pairs of cartridges were dipped. We spiked the second cartridges and used the first two as backgrounds or controls (Slide 15). The results were tabulated in the following slide.

Slide 15



Fifty liters of water was drawn through each resins cartridge by means of peristaltic pumps.

Slide 16

% Recovery of chlorophenols from resins cartridges after pumping through 50 L of pre-filtered Fraser River water acidified to pH 2.

Compounds	Amt spiked	% Rec(1)	Background(1)	% Rec(2)	Background(2)	AV.% Rec.
2,4-Di-	10 ug	107.7	10.7 ppt	104.7	10.7 ppt	106.2
3,5-Di-	10 ug	99.7	0	100.3	0	100.0
2,4,6-Tri-	200 ng	68.7	8.4 ppt	75.5	8.0 ppt	72.1
2,3,5-Tri-	200 ng	93.8	0	125.9	0	109.8
2,3,4,5-Tetra-	200 ng	100.0	27.5 ppt	136.7	32.2 ppt	118.4
2,3,4,6-Tetra-	200 ng	91.7	19.4	100.0	19.5 ppt	95.9
2,3,5,6-Tetra-	200 ng	91.7	19.4	100.0	19.5 ppt	95.9
Penta-	200 ng	108.7	50.6	124.3	49.9 ppt	116.5

Then we decided to do a comparison study of the resins extraction method versus the continuous L/L extraction system. The experiment was done on board ship. During that time, the Survey Division of our Branch was conducting a comparison study on the capabilities of the two centrifuges, the Westfalia and the Alpha Laval. The water coming out of the Westfalia was collected in jugs, acidified with sulfuric acid to pH 2-3, and poured into a clean container from which the water was fed to both systems(Slide 17) . The results were summarized in the following tables (Slide 18 & 19). Since there was one set of the continuous L/L extractor, we could only have one set of recovery for the low and high spikes.

Slide 17

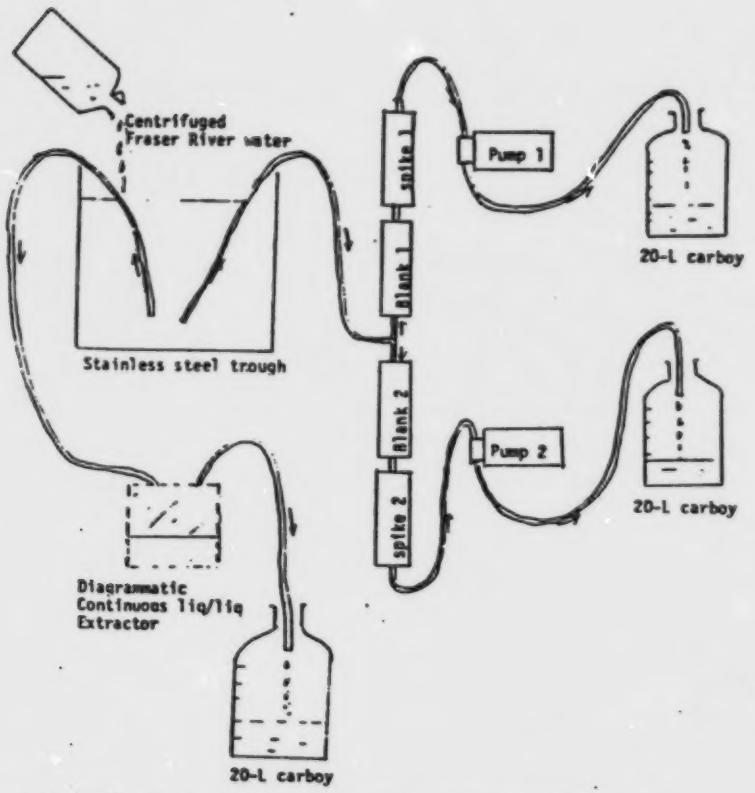


Diagram 2. Comparative study of the resins cartridge technique and the continuous liquid/liquid extraction technique on board ship, July, 1986. Effluent water from the continuous centrifuge, Westfalia, was acidified to pH below 2 before pouring into the stainless steel trough .

Slide 18

Table 3. Recovery (%) of chlorophenols from resins cartridges after elutinn with 50 litres of Fraser River water derived from the Westfalia: low spikes.

Compounds	Amt spiked	% Rec(1)	Backgr(1)	% Rec(2)	Backgr (2)	Av.% Rec.
2,4-Di-	2.5 ug	75.0	185.8 ppt	66.9	205.1 ppt	71.0
3,5-Di-	2.5 ug	102.6		129.5		115.8
2,4,6-Tri-	100 ng	90.6	7.44 ppt	70.1	7.99 ppt	80.4
2,3,5-Tri-	100 ng	132.1		143.4		137.8
2,3,4,5-Tetra-	100 ng	147.1	4.59 ppt	100.0	5.0 ppt	123.6
2,3,4,6-Tetra-	100 ng	140.0	3.99 ppt	117.4	4.31 ppt	128.7
2,3,5,6-Tetra-	100 ng	140.0	3.99 ppt	117.4	4.31 ppt	128.7
Penta-	100 ng	112.8	0.79 ppt	89.7	0.78 ppt	101.3

Table 4. Recovery (%) of chlorophenols from resins cartridges after eluting with 50 litres of FRaser River water derived from the Westfalia: high spikes.

Compoonds	Amt spiked	% Rec(1)	Backgr(1)	% Rec(2)	Backgr (2)	Av.% Rec.
2,4-Di-	20 ug	63.3	66.8 ppt	84.7	69.2 ppt	74.0
3,5-Di-	20 ug	102.7		95.9		99.0
2,4,6-Tri-	400 ng	68.1	8.96 ppt	74.1	9.36 ppt	71.1
2,3,5-Tri-	400 ng	90.0		96.0		93.0
2,3,4,5-Tetra	400 ng	83.3	1.36 ppt	88.9	1.33 ppt	86.1
2,3,4,6-Tetra	400 ng	85.9	2.32 ppt	92.7	2.35 ppt	89.3
2,3,5,6-Tetra	400 ng	85.9	2.32 ppt	92.7	2.35 ppt	89.3
Penta-	400 ng	89.1	2.90 ppt	93.8	0.38 ppt	91.5

Slide 19

Table 5. Recovery (%) of chlorophenols from continuous liq/liq extractor after extracting 50 litres of Fraser River water derived from the Westfalia: low spikes, and high spikes.

Compounds	Amt spiked	% Rec.	Amt spiked	% Rec.
2,4-Di-	2.5 ug	18.8	20 ug	12.1
3,5-Di-	2.5 ug	19.7	20 ug	0
2,4,6-Tri-	100 ng	0	400 ng	31.5
2,3,5-Tri-	100 ng	0	400 ng	53.7
2,3,4,5-Tetra-	100 ng	0	400 ng	71.4
2,3,4,6-Tetra-	100 ng	63.0	400 ng	86.7
2,3,5,6-Tetra-	100 ng	63.0	400 ng	86.7
Penta-	100 ng	375	400 ng	122.2

Note: % Recovery were calculated using the background readings from the resins cartridges studies.

Based on the results thus shown, we have a few comments to make regarding the two extraction methods (Slide 20). Based on 50 L of water the detection limits of the resins method ranged from 200 ppt for dichlorophenols and 4 ppt for the rest of the chlorophenols (Slide 21). Incidentally, the acceptable level for pentachlorophenol in drinking water is about 21 ppb, so we did not see the use of pushing our detection limits any lower.

Some months ago, I was instructed to do another comparison study. This time, the water coming out of the Westfalia was poured into two containers. In one container, the water was basified with sodium bicarbonate and acetic anhydride was added into the extractor so that chlorophenols might be derivatized in situ before extraction. In the other container, the water was acidified as before and passed into two pairs of resins cartridges(Slide 22). Unfortunately, we had some problems with the spiking standards and therefore were unable to compare the results. We are now considering automating our system such that acid may be added by means of a metering pump. Water coming out of the Westfalia will be drained into a container from which the resins cartridges draw their water. In this manner, we hope to be able to study the water compartment of the river simultaneously with the suspended materials in continuous centrifuge over a period of 12-20 hours (23).

Slide 20

Resins cartridge extractor	Continuous liq/liq extractor(CLLE)
Disadvantages	**Advantages**
1 Difficult to control pumping rate because resins sometimes plugged up internal filters.	Easy to control sample flow rate.
2 Resins require four days' effort in purification.	System requires 5-10 minutes solvent wash.
Advantages	**Disadvantages**
1 All components are made of metal and teflon. They are rugged, will stand abuses, and easy to transport.	All components are made of glass; extremely fragile, and difficult to transport.
2 No solvent required during sampling.	Extraction solvent has to be continuously replenished due to solubility in water.
3 Identifal duplicate samples can be achived simultaneously by using a T-splitter.	Duplicate extraction assembly is not only expensive but also labour intensive in preparation and operation.
4 Spike-recovery study showed better extraction efficiency for most of the chlorophenols.	Severe lost of lower chlorophenols occur because of their lower partition coefficient.

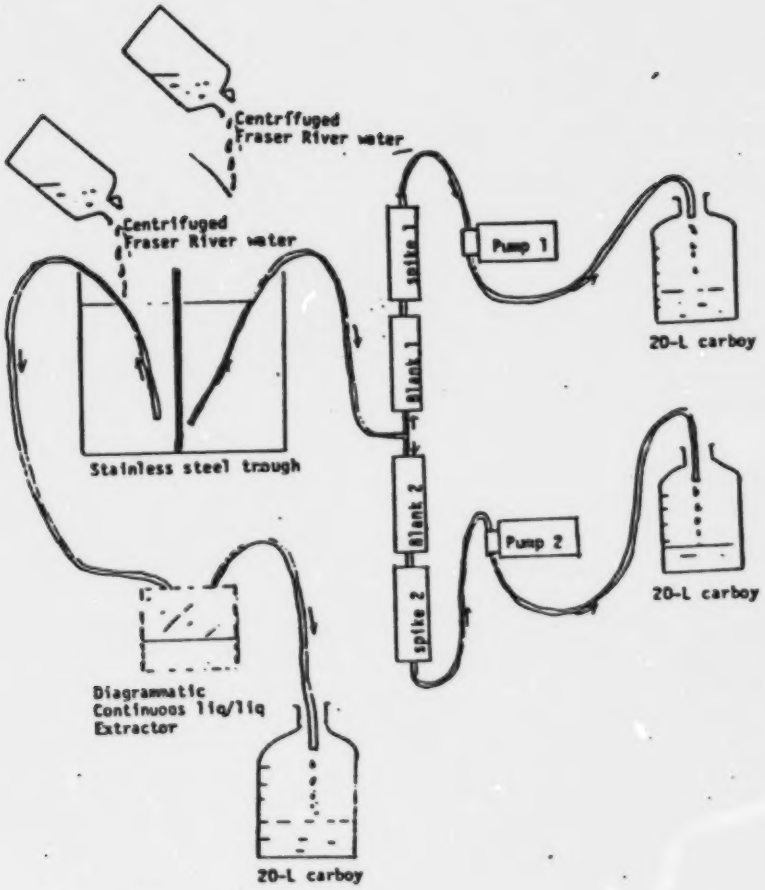
Slide 21

Lowest Detection Limits of Chlorophenols Derived from Resins Method, based on 50-L water sample.

	Det. Limit
2,4-Dichlorophenol	200 ppt
3,5-Dichlorophenol	200 ppt
2,4,6-Trichlorophenol	4 ppt
2,3,5-Trichlorophenol	4 ppt
2,3,4,6-Tetrachlorophenol	4 ppt
2,3,5,6-Tetrachlorophenol	4 ppt
2,3,4,5-Tetrachlorophenol	4 ppt
Pentachlorophenol	4 ppt

Acceptable level for pentachlorophenol in drinking water has been proposed as 21 ppb (Report of the Safe Drinking Water Committee, National Acedemy of Sciences, United States, 1977).

Slide 22



Slide 23

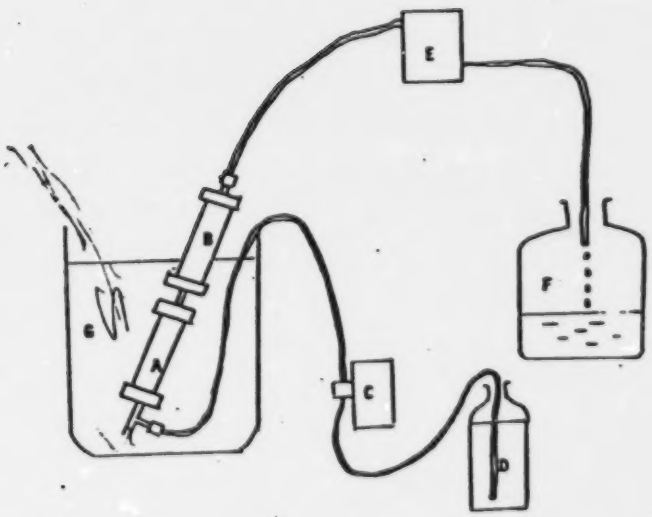


Illustration 2. Single resins cartridge extraction system: A: teflon chips as mixing chamber; B: resins chamber; C: metering pump; D:sulfuric acid; E: Masterflex pump; F: 20-L carboy; and G: 20-L glass trough.

CALIBRATION AND EVALUATION OF THE WESTFALIA CENTRIFUGE AND THE SEAKEM IN-SITU WATER SAMPLER

André Germain

Water Quality Branch

Quebec Region

The effectiveness of the Westfalia centrifuge to retain suspended particles in water as a function of size at different flowrate was evaluated. At less than 10 mg/L of suspended matter recoveries ranged from 92±3% down to 81±1% for input water flow rates of 0.5-6.5 L/min. Regarding the size distribution of particles, an increase in flow rate was responsible for losses of particles with a diameter greater than 2 microns.

The Seakem in-situ water sampler is a 12 mode sampling instrument which can be operated at 3 different sampling rates to pass water through an extraction column. Four of the 12 modes, namely mode 2, 3, 7 and 8 were checked. These sampling modes correspond to different sampling times and intervals. The instrument performed well, the difference between the volume of water pumped and the one indicated by LCD not exceeding 3%.

Different types of columns can be used with the Seakem sampler. Organics can be extracted with a XAD-2 resin or a polyurethane foam, metals by a hydroxyquinoline-bonded silica, and mercury by a dithizone impregnated polyurethane foam.

A) GROUPE ELECTROGENE

1 Génératrice ONAN 5,0 cck - 5 - DR
2 Réservoir à essence 5 gals.
3 Boîte de distribution
4 Démarreur pour centrifugeuse Westfalia
5 Interrupteur pour pompe submersible
6 Démarreur et coupe-circuit pour pompe submersible
7 et 8 Prises auxiliaires 120 V

B) SYSTEME D'ADDUCTION ET DE DISTRIBUTION D'EAU, D'ECHANTILLONNAGE DES SUSPENSOÏDES ET D'ABSORBTION SUR COLONNE DE RESINE XAD-2

9 Flotteur
10 Pompe submersible (Grunfos sp 1-9)
11 Conduite principale (Teflon "pfa")/4"ϕ)
12 Module de régulation de la pression et trop-plein
13 Robinet à pointeau de régulation du débit
14 Rodamètre (Brooks 1112)
15 Centrifugeuse Westfalia
16 Support à filtre 142 mm et trop-plein
17 Colonne de résine XAD-2
18 Echantillonneur Seastar

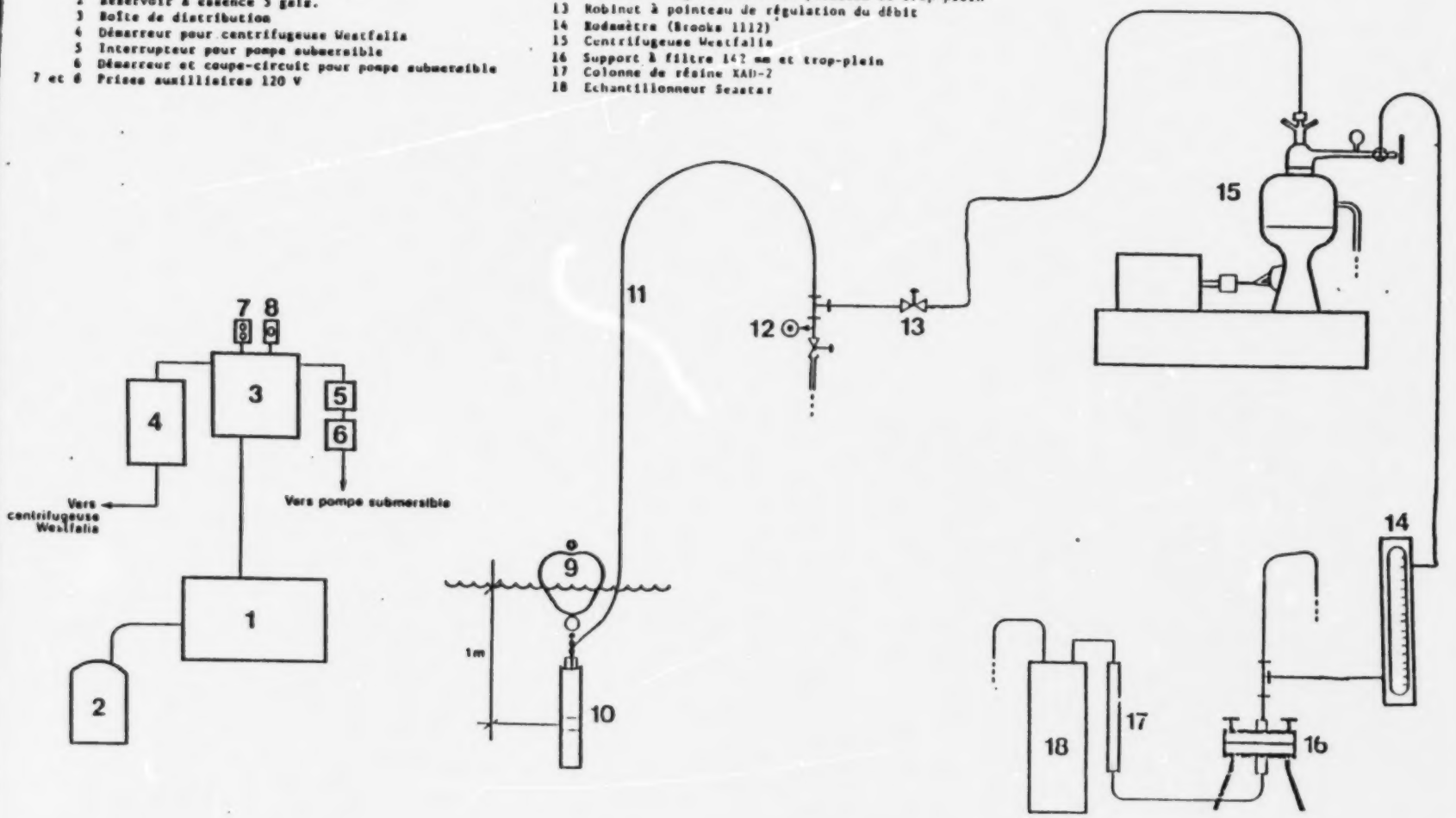


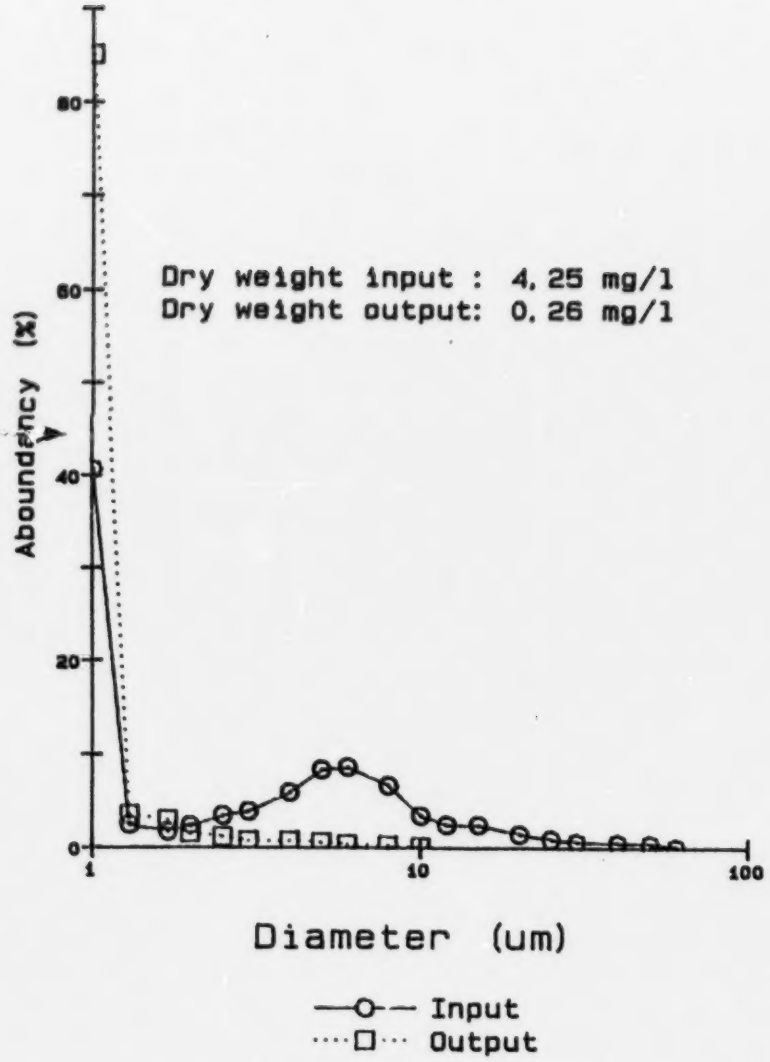
Schéma du système d'échantillonnage monté en série

The performance of the XAD-2 resin column for PCBs and 19 chlorinated pesticides was checked as well as the influence of volume of water pumped and the flowrate on the recovery of those compounds. Ten, 18 and 36 liters of spiked water, each of these at 3 different flowrates (50, 100 and 150 mL/min), were pumped through the resin. The concentration for each compound in the spiked water was 10 ng/L. Excluding heptachlor, aldrin, p,p'-DDT and β-BHC, there was no influence observed for the flowrate used or the volume pumped. The mean recovery for organochlorines was 94±19% and 80±13% for PCBs. The waster used to do this recovery study was Millipore "Super-Q", therefore there was no need to filter it with a glass-fiber filter, as done in the field work.

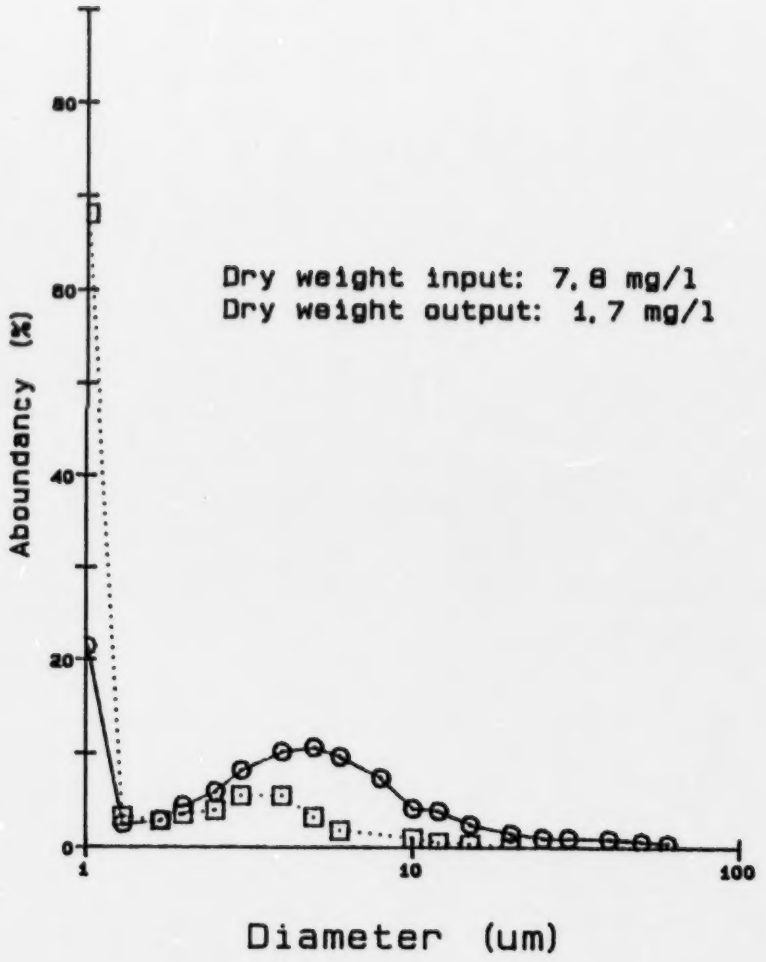
Following the calibration, some field essays were carried out. The Westfalia centrifuge and the Seakem in-situ water sampler were coupled in series and both performed as expected. Clarified water was brought to the Seakem. PCBs and some OCs were found in both suspended sediment and water. After the 1985 field essay, recovery check with the Seakem using a glass-fiber filter, as recommended by Seastar Instrument Ltd, was done. Surprisingly, the glass-fiber filter retained 20-100% of almost all of the compounds spiked in water. Only BHCs, the two endosulfan isomers, endrin and dieldrin were recovered at the 100% level. The filter was changed for the 1986 and 1987 field trips.

In conclusion, the centrifuge operates well in field conditions, the mechanical parts of the Seakem function properly, and the chemical part seems to be alright, if glass-fiber filters are replaced by polypropylene filters.

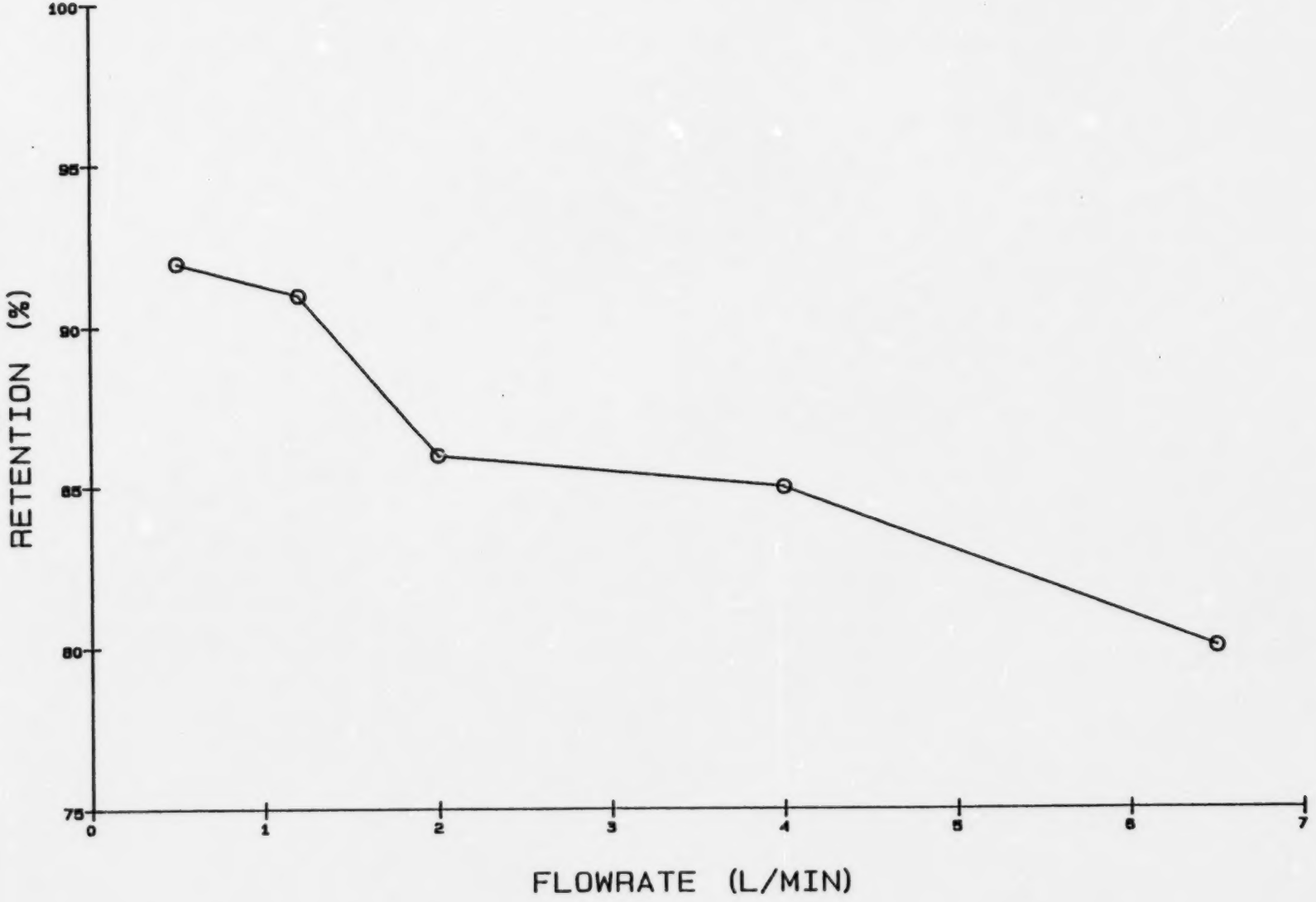
PARTICLE SIZE
(0.5 l/min)



PARTICLE SIZE
(6 l/min)



RETENTION VS FLOWRATE



SEASTAR'S CHARACTERISTIC

MODE	SAMPLING TIME (hours)	ON/OFF CYCLE (hour)	VOLUME PUMPED AT 50 ml/min	FLOW 100 ml/min	RATE 150 ml/min
2	100	100/0	300	600	900
3	100	0.5/0.5	150	300	450
7	2	2/0	6	12	18
8	8	8/0	24	48	72

CALIBRATION OF MODE 2

TIME (min)	VOLUME ON LCD	PUMPED VOLUME (L)	variation
6.67	1.01	1.00	+1.0
33.67	5.01	5.00	+0.2
68.67	10.02	10.00	+0.2
103.33	15.06	15.00	+0.4
137.00	19.96	20.00	-0.2

FLOWRATE OF 150 ml/min

EXPERIMENTAL CONTROLS

ITEM	AVERAGE RECOVERY %	RANGE %
LIQUID-LIQUID EXTR.	98 ± 7	72-102
2nd ELUTION	0.7 ± 1.4	0-5
2nd COLUMN	2.0 ± 3.0	0-12
RINCE OF CONTAINER	3.3 ± 4.0	0-20
BLANK	2.4 ± 2.5	0-10

EXPRESSED AS % OF SPIKING CONCENTRATION USED

RECOVERY

COMPOUND	LITTERATURE	GREEN & KOWALSKI	OUR RESULTS n = 27
PCB	89 ± 7	91 ± 12	80 ± 13
HCB			92 ± 43
HEPT.	85 ± 14	69 ± 4	74 ± 21
ALDRINE	67 ± 24	75 ± 2	68 ± 16
pp'DDE	85 ± 14	92 ± 10	95 ± 23
MIREX	97.		75 ± 10
a-BHC	64 ± 16		87 ± 9
LINDANE	63 ± 26	89 ± 12	86 ± 13
b-BHC	71.		53 ± 23
HEPT. EP.	73.	83 ± 8	96 ± 9
a-CHLORDANE	92.	74 ± 4	96 ± 8
g-CHLORDANE	91 ± 2	78 ± 8	95 ± 9
op'-DDD			92 ± 6
op'-DDT	92 ± 5		102 ± 26
pp'-DDD			86 ± 8
METHOXYCHLOR	108.	91 ± 10	143 ± 48
DIELDRINE	84 ± 16	82 ± 7	88 ± 6
ENDRINE	90 ± 8	82 ± 16	117 ± 15
b-ENDOSULFAN			61 ± 6
AVERAGE MEAN	83 ± 13	82 ± 8	88 ± 19

DETECTED COMPOUNDS

Compound	CONC WATER ng/l	FREQUENCY % n=11 or 18	CONC SEDIMENT ng/g
PCB	<0.2-2.3	33	1-150
HCB	<0.03-0.9	28	2-6
a-BHC	<0.03-4	94	<1-2
b-BHC	<0.02-0.4	38	<1
a-CHLOR	<0.02-1.9	64	<1-5
g-CHLOR	<0.02-0.06	27	<1-7
op'-DDD	<0.1-8.8	9	<1-20
pp'-DDD	<0.1-0.2	11	<1-9
pp'-DDT	<0.1-0.8	27	<1-8

REFERENCES

Roche et Associés Ltée, juin 1985. Mise au point de l'application de la méthode de centrifugation en continu pour l'éechantillonnage des solides en suspension et de la méthode de pompage à travers une colonne de résine adsorbants pour l'éechantillonnage de l'eau. 123 p. (Couture, R., Caron, J., Leblanc, R.).

Couture, R., et J. Caron, mai 1986. Mise au point de l'application de la méthode de pompage à travers une colonne de résine adsorbants pour l'éechantillonnage de l'eau. Les consultants Sogeam Inc. 94 p. plus annexes.

DEVELOPMENT OF AN AUTOMATED CONTINUOUS-FLOW FIELD SAMPLER FOR TRACE ORGANIC CONTAMINANTS IN SURFACE AND GROUND WATERS

Eric Harrison and Henry Behmann

ZENON Environmental Inc.

Summary

A field transportable continuous organics extraction system is described. The system includes modules to collect both volatile and extractable organics. Non-volatile organics are extracted by a continuous counter-current miniature Karr column. This liquid-liquid extractor provides extraction efficiency which exceeds that of EPA Method 625, especially for low p-value compounds. An integrated volatiles sample is collected in conjunction with the extractables and sparged onto a multicomponent trap. The extract and the trap, together, permit broad spectrum characterization of the sample. A microcomputer provides for setting and control of pH, sample flow rate and volume, start-up and shut-down of the process, and a printed record of the sample conditions. An ancillary module is under development to recover and recycle dichloromethane (DCM) from the sampler effluent.

System Description

A simplified block diagram of the system is given in Figure 1. The feed water is pumped past both the volatiles collector (trap) and

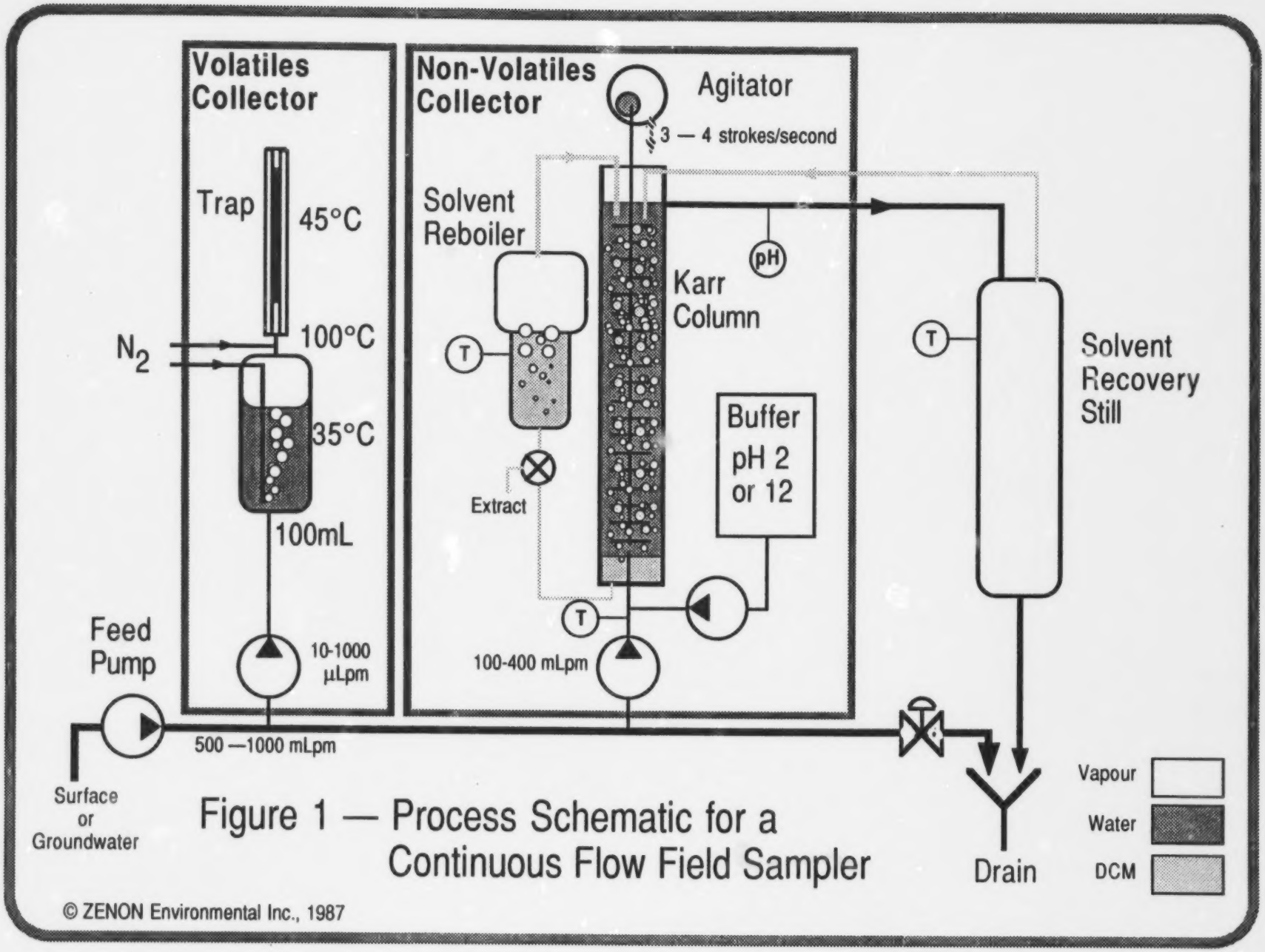


Figure 1 — Process Schematic for a Continuous Flow Field Sampler

non--volatiles collector (Karr column) portions of the system, then to drain. The trap is contained in a separate frame and is set up as far away from the Karr column as possible to minimize contamination by DCM vapour. The main frame contains the Karr column, control microcomputer, solvent reboiler, and associated pumps and reservoirs. A third frame contains the solvent recovery still. Each frame weighs approximately 20kg, dry, and is designed to be set up and interconnected quickly and conveniently. Total power consumption is less than 3 kW.

The trap is controlled by the microcomputer in the Karr column unit. The volatiles sample is pumped into a 100 mL vial at such a rate that 100 mL is collected during the sample time, i.e. for a 72 hr sample time, the rate is 23 µL/min. The sample vial is maintained at 35°C during the entire sampling period. The trap is continuously purged with zero gas N_2 at 50 mL/min to prevent adsorption from the atmosphere and help to remove any water vapour which may accumulate on the trap. At the end of the sampling interval, the sample is sparged for a predetermined time. The trap is then removed and capped. A variety/mixture of sorbent materials may be used depending on the target compounds of interest. In the laboratory, the sample is analysed by thermal desorption into a GC or GC/MS.

The non-volatile compounds are extracted using a counter-current Karr column. Water is pumped upward through the column and DCM flows downward by gravity. Several plates in the column are reciprocated at a

rate such that a uniform dispersion of fine DCM droplets is maintained throughout the active length of the column. The ratio of water to solvent is set to about 10:1. Fresh solvent is provided by the reboiler unit which is controlled to give a fixed solvent flow rate. About 500 mL of solvent is retained in the reboiler bottoms and serves as the extract at the end of the run.

The microcomputer controls the operation of the unit from start-up to shut-down. The operator needs only to set up the unit(s); place the bottles of DCM and buffer in the holders; select the desired pH, flow rate and sample time; and push "run". The unit then adds DCM to the column, tops up with water, starts and stabilizes the reboiler, and begins the collection both volatiles and non-volatiles. At the end of the run, the system is shut-down in a similar orderly fashion.

Performance

To date, the system has undergone intensive engineering testing. The performance testing has been carried out using spike solutions at concentrations normally found in environmental samples. Controlled experiments have been run using test compounds with a wide range of partition coefficients (p-values), as well as a wide range of operationing conditions. When solvent hold-up volume and the agitation rates are optimal, the system extraction efficiency exceeds that of the normal laboratory three pass manual extraction, and appears to perform even better for low p-value compounds.

The 50 cm column provides between three and four equilibrium stages. One set of experiments was run comparing the extraction efficiency of 50 cm and 80 cm columns. The mean difference in the extraction efficiency between the two columns was < 5%, which is statistically insignificant.

The system is scheduled for evaluation in the field later this summer.

Conclusions

The Karr column based extraction system is unique among field samplers in that it provides multiple extraction stages, integrates both volatiles and non-volatiles collection, and is totally computer controlled. The engineering testing indicates that it has the potential to efficiently and consistently collect otherwise hard to recover environmental contaminants.

SAMPLING AND EXTRACTION OF LARGE VOLUME WATER SAMPLES FOR TRACE ORGANIC ANALYSIS

K.W. Kuntz, P.D. Goulden, J. Biberhofer and D.H.J. Anthony

Canada Centre for Inland Waters

Burlington, Ontario

ABSTRACT:

A sampling system has been developed for the collection of water and suspended sediment samples. Incorporated in this system is a liquid-liquid counter current extractor which is capable of extracting large volumes of water for trace organic analysis. The extraction device is capable of performing extractions on discrete samples or operating in a time integrated continuous flow mode for periods of 24 hours or longer. Its use has resulted in a significant reduction in detection limits. The paper describes the operation and usage of the counter current extractor for 24-hour continuous on-site extraction, surrogate spiking regimes presently used, and some Great Lakes Surveillance Cruise recovery data. Potential for other field applications as well as some advantages and future improvements to this system are also discussed.

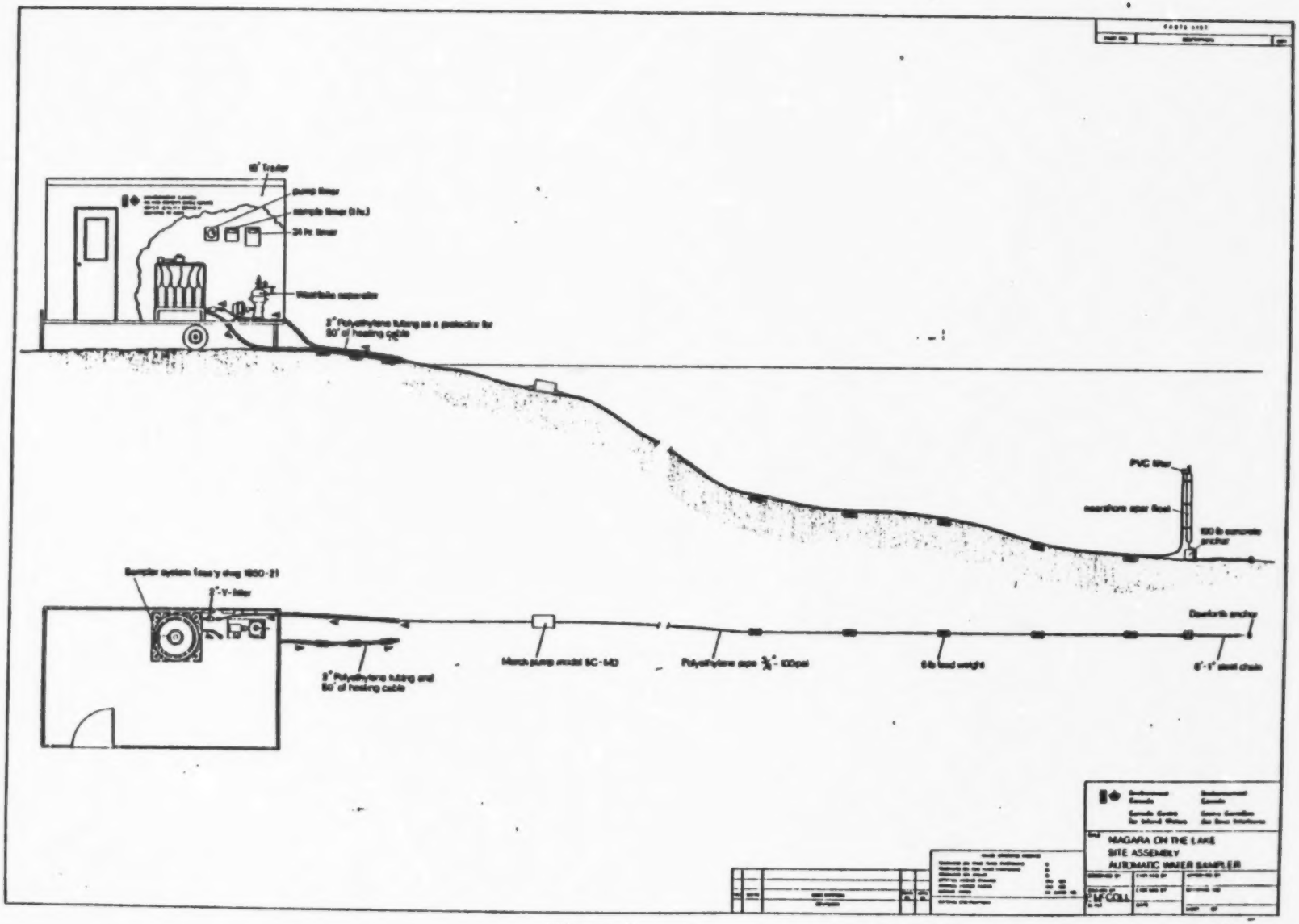

PVC filter
nearshore spar float
Bubbler system (assy drwg 1800-21)
Manta pump model SC-MD
Polyethylene rope
6 lb lead weight
Dietrich anchor
MAGARA ON THE LAKE
SITE ASSEMBLY
AUTOMATIC WATER SAMPLER

Figure 1

I) Water Quality Sampling System

The sampling system consists of three basic components: a. intake line and pump, b. suspended sediments sampler (Westfalia centrifuge), and c. organic contaminants extractor. The intake line and the pump are submerged, while the samplers are housed in a trailer on the river bank.

a. Intake Line and Pump

The intake line (Figure 1) is composed of a 3/4 inch (1.9 cm) id polyethylene tube placed in the river. The tube is anchored to shore with a 1/4 inch stainless steel cable and is weighted so as to settle onto the bottom of the river. The tube is connected to an anchored spar buoy thus allowing the sample intake to float freely up from the river bottom. At the end of the last section of polyethylene tube there is a polyethylene plug with a series of 1/4 inch holes acting as a coarse filter to prevent fish and weeds from entering and fouling the intake. To collect samples in winter, the first 25 ft of the intake, from the trailer to the submerged pump, is wrapped with a heating cable to prevent freezing.

A magnetic drive, submersible pump with ceramic impellor (March 5C-MD) is used to pump the water up to the samplers in the trailer. This pump has a capability of up to about 20 L/min at a head of about 2 metres.

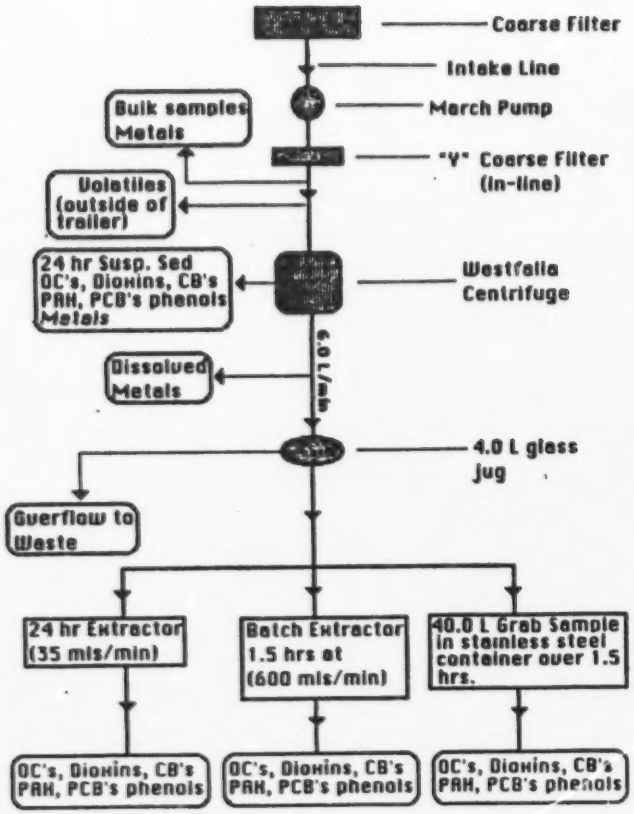

Coarse Filter
Intake Line
March Pump
Bulk samples Metals
"Y" Coarse Filter (in-line)
Volatiles (outside of trailer)
24 hr Susp. Sed OC's, Dioxins, CB's PAH, PCB's phenols Metals
Westfalia Centrifuge
Dissolved Metals
6.0 L/min
4.0 L glass jug
Overflow to Waste
24 hr Extractor (35 mls/min)
Batch Extractor 1.5 hrs at (600 mls/min)
40.0 L Grab Sample in stainless steel container over 1.5 hrs.
OC's, Dioxins, CB's PAH, PCB's phenols
OC's, Dioxins, CB's PAH, PCB's phenols
OC's, Dioxins, CB's PAH, PCB's phenols

Figure 2 Niagara River Sampling System

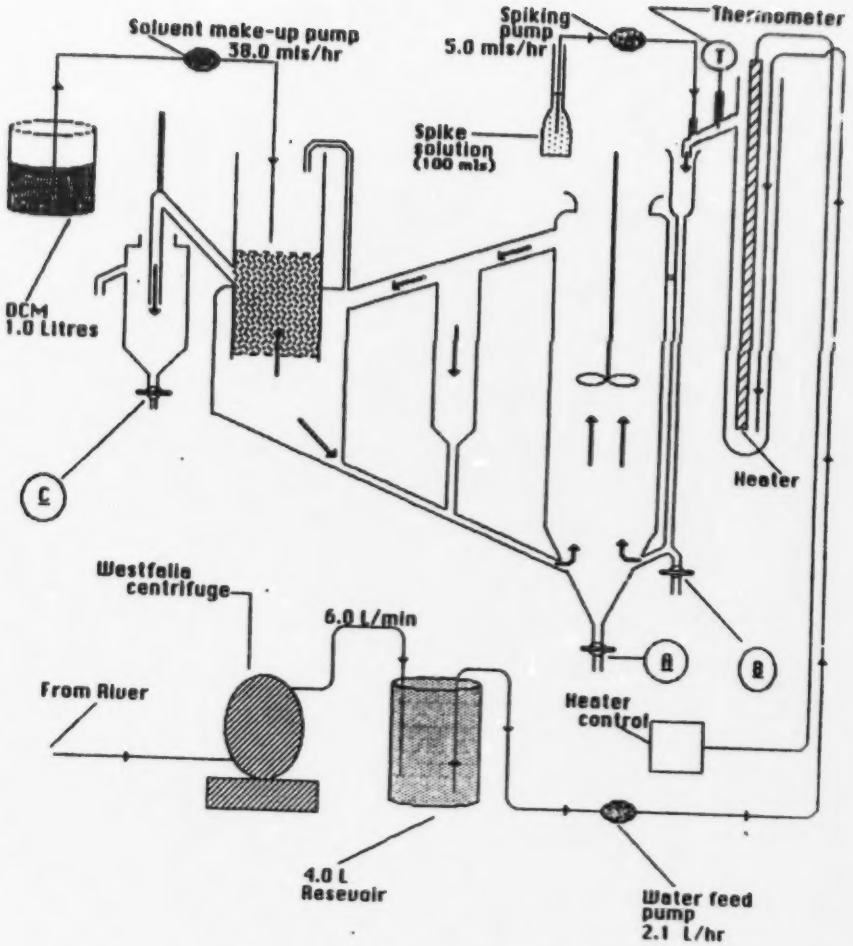


Figure 3. Counter-current Extractor

b. Suspended Sediment Sampler (Westfalia Centrifuge)

Suspended sediments are collected with a continuous flow separator, Model KA-02-06-075 Westfalia Centrifuge. A four-chamber, all stainless steel (No. 316) bowl is used to collect the suspended sediments. Bowl speed, when driven by the 1745 rpm motor, is 9470 rpm generating a centrifugal force of 9500 g. The bowl volume is 1.9 L and the bowl sediment space with the four chamber inserts is 1.0 L. The residence time of any parcel of water at 6 L/min flowrate is about 20 seconds.

c. Organic Contaminants Extractor

Design

This extractor was developed in a joint programme between the National Water Research Institute (NWRI) and the Water Quality Branch - Ontario Region (WQB). It can be used for 24-hour collection in the field and it can heat the water sample to about 20 deg. C. This temperature is necessary for efficient extraction and separation of the solvent-water phases. It also prevents gases from coming out of solution and carrying the dichloromethane (DCM) out of the extractor. A schematic of the sampling scheme is shown in Figure 2.

This extractor (Figure 3) is in essence a mixer-settler in which the water sample is continuously passed through an agitated vessel containing the solvent (DCM). The solvent settles from the effluent water back into the mixer and the effluent water then passes to waste.

The purpose of the stirrer in the mixing chamber is to give efficient mixing and to minimize the formation of the emulsion. The agitator is a three bladed propeller with a steep pitch operated at approximately 800 rpm. DCM is slightly soluble in water. Thus the effluent contains dissolved DCM and there can be some loss of DCM due to its volatility. The combined losses amount to about 1.5% of the volume of the water extracted. To compensate for the solvent losses, a supply of fresh DCM is added at a predetermined rate into the packed column part of the extractor. The column, filled with "Teflon" raschig rings, provides a scrubbing mechanism for the effluent water using the counter current created by the fresh DCM. This column serves three purposes:

i) to help break up emulsions

ii) to scrub out any remaining droplets of solute containing solvent

iii) to extract any remaining organics from the effluent water

Extractor validation

Several experiments were run with two extractors arranged "in tandem", i.e. one after the other. Anthracene was spiked into the first

extractor along with the five surrogate compounds* and then the second extractor was used to determine if any of the anthracene or the surrogates were present in the effluent water from the first extractor. The five surrogates were 1,3-dibromobenzene, 1,3,5-tribromobenzene, 1,2,4,5-tetrabromobenzene, 2,3,5,6-tetrachlorobiphenyl and endrin ketone. All these compounds are essentially absent in the aquatic environment of the Lakes Basin. The exact point of extraction process and the purpose for which the surrogates are added are shown in Table 1.

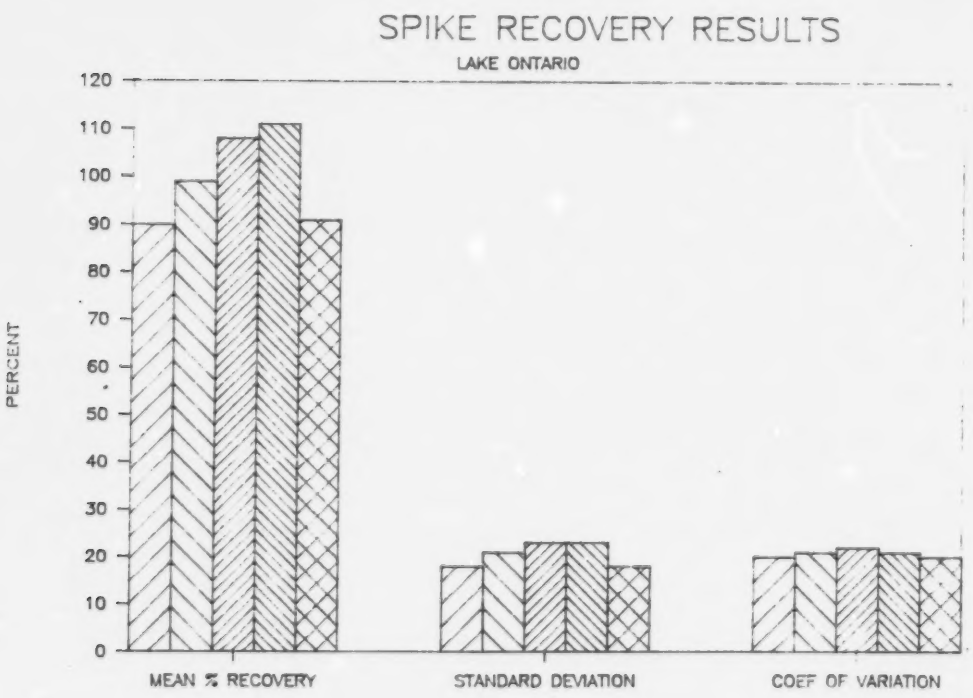
Five 24-hour replicate extractions in the lab using anthracene as a tracer indicated that the efficiency of the first extractor was greater than 99%. Results from a set of seven "tandem" field extractions indicated that for the twenty eight compounds analysed (including CB's, OC's and PCB's), for a total of 196 measurements, there were only 24 (or 12%) positive results in the second extracts. Of those, only four were greater than 0.08 ng/L and none were greater than 0.5 ng/L. The percent recoveries were below 90% for only 6 of the 196 determinations.

*A surrogate compound is a substance not usually found in the environment but which is chemically similar to an environmental contaminant. This similarity allows the use of surrogates as internal standards in organic analytical procedures. They are used, for example, to determine recoveries and to adjust the retention times of gas chromatographic methods.

Table 1

NEW SURROGATE SPIKING REGIME

SURROGATES ADDED	WHERE ADDED	PURPOSE
1. DELTA BHC	FIELD EXTRACTION	MONITOR EXTRACTION EFFICIENCY
2. 1 3 5 TRIBROMOBENZENE	"	"
3. 1 2 4 5 TETRABROMOBENZENE	"	"
4. 1 3 DIBROMOBENZENE	PRIOR TO LAB CONCENTRATION	MONITOR VOLATILITY LOSSES DURING EVAPORATION
5. ENDRIN KETONE	PRIOR TO CHROMAT. FRACTIONATION	MONITOR ANALYTICAL CLEANUP PERFORMANCE
6. 2 3 5 6 TETRACHLOROBIPHENYL	"	"
7. OCTACHLORONAPHTHALENE	PRIOR TO GC-EC	MONITOR SYSTEM RESPONSE



Since February 1987 only three surrogates (delta-BHC, 1,3,5-tribromobenzene and 1,2,4,5-tetrabromobenzene) are added to extractor in the field to monitor extraction efficiency, volatility and entrainment.

Prior to concentration of the DCM and solvent replacement with iso-octane, 1,3-dibromobenzene is added to the extract to monitor the volatility losses during the evaporation phase of the analysis. Endrin ketone and 2,3,5,6-tetrachlorobiphenyl are added to the non-polar concentrate prior to open column chromatographic fractionation to monitor analytical performance throughout the sample cleanup phase. Finally, octachloronaphthalene is added to the final extract, immediately prior to GC-ECD determination, as an aid to normalizing system response throughout the gas chromatography steps.

Of the three surrogate spikes added in the field, levels up to 0.016 ng/L were found in less than 20% of the extracts from the second extractor; all other results were "not detected". The recovery, by the first extraction, for field spikes was greater than 98%.

The results from another experiment, consisting of the collection of eight consecutive samples, in duplicate, over about a 20-hour period at Niagara on the Lake, the splitting and recombining of the extracts for four different sets of analyses, followed by spiking of the extracts with known amounts of OC's, CB's and PCB's as well as the normal surrogates, indicated that the variability between the two samplers was minimal and that the coefficient of variation (CV) over the

20-hour period did not exceed 30%, except for a few parameters such as heptachlor, p,p-DDT, methoxychlor and PCB's. Of the 28 parameters measured, 17 had a CV of less than 20%. All of the surrogate spikes added also had a CV of less than 20%, except for octachloronaphthalene.

Mean % recoveries of the surrogate spikes added to samples collected during a consecutive 7-day sampling program, at Niagara-on-the-Lake, were:

1,3-dibromobenzene	95%
1,3,5-tribromobenzene	86%
1,2,4,5-tetrabromobenzene	101%
2,3,5,6-tetrachlorobiphenyl	115%
delta-BHC	179% (high because is native)
endrin ketone	107%
octachloronaphthalene	112 & 99% (added in the laboratory to two different fractions)

A modified sampler was used on Great Lakes Surveillance cruises on Lakes Ontario, Erie, Huron, Georgian Bay and Superior in 1986. The percent recovery and the CV for the Lake Ontario results (37 samples) were:

Surrogate	No. of Results	% Recovery	SD	CV
1,3-dibromobenzene	37	90	18	20
1,3,5-tribromobenzene	37	99	21	21
1,2,4,5-tetrabromobenzene	37	108	23	22
2,3,5,6-tetrachlorobiphenyl	36	111	23	21
Endrin ketone	37	91	18	20

Other Applications

As already mentioned this extractor has been used aboard the research vessel CSS Limnos to extract large volumes (up to 50 L) of Great Lakes water for organic contaminants analysis.

The system has been modified for continuous use over a seven day period. Depending on the objectives of the sampling program, the extract can be collected each day or composited for a week.

The extractor is transportable and with care it can be operated from the back of a truck for sampling of streams, rivers and other bodies of water at remote locations.

The extractor can also be used to extract large volume water samples in the laboratory. The heater is not necessary if the water is at room temperature.

Advantages of the extractor

1. Extracts large volume of water thus increasing the detectability of trace level compounds.
2. Uses small volume of solvent.
3. Is rugged and portable.
4. Every sample has surrogate spike recovery data.

Future improvements

1. The system will be enclosed to prevent operator exposure to DCM vapours. A magnetic stirrer will be used instead of the present stirrer. This should further reduce the possibility of external sources of contamination as well as reduce volatilization without reducing the efficiency of the extractor.

2. A solvent recovery system is proposed to recover the dissolved or entrapped DCM from the effluent water and reduce the amount of DCM needed for solvent makeup.

EVALUATION OF SAMPLERS FOR COLLECTION OF PRECIPITATION FOR ANALYSIS OF ORGANIC COMPOUNDS

Steven J. Eisenreich
Environmental Engineering Sciences
Department of Civil and Mineral Engineering
University of Minnesota
Minneapolis, MN 55455

The performance of the precipitation samplers was evaluated during the rainy season of 1986 with some measurements made in the latter part of 1985. On average, the precipitation samplers collected 95% of the rain gauge values, if periods during which mechanical problems occurred were excluded. The precipitation samplers experienced several types of problems as listed below:

- precipitation overflow (bulk solvent sampler)
- rain sensor malfunction (resin Aero Chemetric)
- blown fuse (MIC sampler)
- vandalism
- failure of mechanical connections on movable arm (MIC sampler)

The performance of the MIC sampler makes it suitable for a monitoring program in which samples are collected bi-weekly.

The performance of the samplers was rigorously evaluated by their ability to produce comparable concentrations (event, volume-weighted) of 14 selected compounds. The compounds of interest were 4 PAHs, total PAHs, 5 PCB congeners, total PCBs, p,p'-DDE, HCB and 1,2 4-trichlorobenzene.

The mode of concentration of the compounds was an important determinant of the final result. The SM sampler isolated the organic compounds in the field by passage of the water through 200 mL DCM sitting at the bottom of a brown 4 L bottle. The MIC samplers isolated the organics of interest using XAD-2 resin cartridges with an without prior filtration. The results suggest that either technique may be applied successfully to the quantitative isolation of trace organics in the field. XAD resin has a higher "blank" concentration than the SM sampler but it is better suited for collecting large rainfalls. Although the samplers equipped with XAD resin cartridges provided comparable results, the long-term solution to both blank and overflow problems may be to use an "active" version of the SM sampler or perhaps to use a different adsorbent such as Tenax.

The final results of this study are now being assembled in a final report to the GLNPO of the U.S. EPA.

MONITORING OF TRACE ORGANIC CONTAMINANTS IN WET PRECIPITATION

C.H. Chan

Water Quality Branch - Ontario Region

The design and use of a year round wet-only precipitation collector for trace organic contaminants analyses are described. The sampler is electronically controlled and features a .25 square meters stainless steel funnel with a 4-L amber glass bottle. The whole assembly is insulated and is equipped with heating elemets for ice/snow collection. The samples are preserved in-situ with methylene chloride. A small network of four sampling stations was established in the Great Lakes Basin. A total of 97 rain/snow samples were collected from the network during 1986. These samples were analyzed for sixteen organochlorine pesticides, ten chlorobenzenes, and twelve polycyclic aromatic hydrocarbons. The most significant organochlorine polycyclic aromatic hydrocarbons. The most significant organochlorine pesticides found were alpha and gamma-BHC and methoxychlor with mean concentrations in the range of 7-10 ng/L, 4-5 ng/L and 2-7 ng/L, respectively. Other organochlorine pesticides were detected ocassionally at the subnanogram levels. Polychlorinated biphenyls were also widely detected with mean concentrations of 7-10 ng/L. Mean concentrations of dichlorobenzene ranged from 2 to 19 ng/L. Polycyclic aromatic hydrocarbons were detected in about 50 percent of the sample, the prevalent mis being phenanthrene, 2-methylnapthalene, fluorene and pyrene measured at 50-200 ng/L.

SUMMARY OF DISCUSSION - PANEL SESSION

The discussion focussed on the use of continuous liquid-liquid extraction and resin adsorption methods for isolation and concentration of trace organics from large volumes of waters. The continuous liquid-liquid extraction systems using methylene chloride and the use of XAD-resins were preferred over other isolation methods. XAD-2 resin was preferred over other adsorbants (carbon, tennax, C_{18}-ODS) because the adsorption on XAD-resins is believed to be due to Van der Waals forces and hence quantitative elution of the compounds from an XAD-2 resin should easily be accomplished by simply washing the resin bed with solvent. Dr. S. Eisenreich noted, however, that for precipitation sample concentration Tennax may be preferred to an XAD resin and that work investigating this aspect is now underway.

Variables affecting the performance of both the continuous liquid-liquid extraction and resin column adsorption systems were discussed. These included the theory of processes, parameters affecting concentration efficiency, capacity and effect of background composition, artifacts and blanks.

This is a brief summary of the discussions and conclusions from the panel session which followed the individual presentations.

Concentration Processess

Concentration of organic compounds in liquid-liquid extraction systems is defined by partition coefficients. Hence, the extractability of any compound can be theoretically predicted from the partition coefficient of a compound between the water sample and an organic solvent. On the other hand, XAD-resins concentrate contaminants by adsorption. It is possible to predict the performance of the resin for single compound in distilled water using frontal chromatography. However, the adsorption cannot be theoretically described for a complex solute mixture and environmental sample matrix with complex chemical composition.

Concentration Efficiency

The efficiency of samplers employing macro-reticular resins has been found to be a function of resin type and amount, column dimension, water flow rate, elution solvent, etc. In addition, the efficiency also depends on the type of compounds present in the sample, their range of concentrations and the presence of high molecular weight molecules.

The concentration efficiency employing liquid-liquid extraction can be determined as long as the partition coefficients are known and the percent recovery has been determined. In addition, the selectivity and efficiency of the extraction procedure can be optimized by choice of solvent and by adjusting solvent to water ratio and pH of the water sample. Furthermore, in a continuous liquid-liquid extraction system it is possible to re-use the solvent (solvent recycling by reflux) to extract large volumes of water sample with the same and, hence, relatively small volume of solvent.

Capacity

Resins and other adsorbants are known to have limited capacity to concentrate organic compounds. XAD-resins are relatively non-specific and adsorb a wide variety of compounds such as alcohols, esters, hydrocarbons, pesticides, herbicides and polynuclear aromatic hydrocarbons. Therefore, it is possible that certain trace contaminants in the presence of large concentrations of other organic substances may not undergo quantitative adsorption. In fact, a "breakthrough" of trace organic contaminants in the presence of relatively higher concentration of DOC is known to occur. It is believed that DOC competes for the adsorption sites thus causing the breakthrough of the trace organic contaminants that need to be concentrated for analysis.

Humic acids are reported to clog the pores of XAD-2 resins resulting in a low retention capacity for other trace contaminants of interest. The presence of humic acids is also known to affect the extractability of certain contaminants using liquid-liquid extraction systems. However, the effect is not as pronounced as in the case of resin extractions and, thus, they can concentrate trace organics in presence of higher concentrations of other chemical compounds in a sample. Furthermore, in a liquid-liquid system the presence of high concentrations of these other chemical compounds does not significantly affect the extractability of non-polar trace organics.

Artifacts and Blanking Problems

Artifacts from resins are reported to occur when the XAD-resin extract is analyzed by capillary column gas chromatography. Artifacts

are also known to take part in competitive adsorption during sampling, which can cause breakthrough of compounds of interest.

Resins can produce high blanks. To avoid blank problems and minimize artifacts, they require extensive cleaning, controlled storage and preservation.

Some artifacts are known to exist when methylene chloride is used as a solvent in liquid-liquid extraction. These are attributed to the contamination of the solvent or due to the preservatives added to the solvent. These can be minimized by either replacing methylene chloride with other solvents such as Freon FC-113 or by the use of freshly distilled solvent.

CONCLUSIONS AND RECOMMENDATIONS

Liquid-liquid extraction was considered as a superior quantitative technique for extraction of trace contaminants from large volumes of water samples. XAD-resins have the potential of being used as a screening technique, capable of providing semi-quantitative analysis. In cases where it is impractical to use liquid-liquid extraction, the resin-column systems can be optimized to provide quantitative analysis. The optimization must be undertaken for each project. It consists of evaluation of such factors as the type of resin, size of column, flow rate, efficiency of extraction, capacity, "breakthrough" of the organic substances, artifacts, blanks and cleaning procedures for the resins. Some of these factors must also be optimized in the case of liquid-liquid extraction.

Responses to the Three Specific Questions Posed

The three specific questions were:

a) What are the advantages and limitations of each technique? What precautions should be taken in their applications?

b) For given situations, which is the preferred technique? Provide guidelines and rationale for each case.

c) Is further research and development required? Which areas should be addressed on a priority basis?

In addressing the first two questions, participants agreed to the following specific observations and recommendations:

- Regardless of which technique is applied, the analytical process must be carefully designed to fit the objectives of the study, i.e. the specific use of the data must be first established.

- Dichloromethane blanks are of concern and should be carefully controlled. In the liquid-liquid extraction application, blanks should be run before every extraction.

- In the liquid-liquid extraction (LLE) application, it is advisable to use the solvent recycling technique wherever practicable.

- Resins should not be re-used once sample extraction has taken place.

- Suspended materials and high humic acid content of samples may result in (i) rapid clogging of the resin column and (ii) may affect extraction efficiency and effectiveness of both resin and liquid-liquid extractions.

- Back-up columns are necessary whether the LLE or resin extraction technique is being applied.

- For non-target contaminants, LLE affords quantitative measurements while the resin extraction affords, at best, only semi-quantitative measurements.

- The resin extraction technique facilitates the simultaneous deployment of a series of extractors over specified time periods. Also, resin extractors can be employed in remote areas where it is impracticable to use liquid-liquid extractors.

- It is essential that surrogates be spiked at different stages in the sample extraction/analysis process.

The following comments and recommendations were compiled in response to the third question.

- The humic substance phenomenon needs to be researched.

- The feasibility of the routine application of super-critical fluid extraction techniques for sample preconcentration should be explored.

- The LLE precipitation sampler in current use by Environment Canada, should be optimized by incorporating certain design changes.

- Research leading to a better understanding on how resin columns operate is needed.

- The colloidal effects on both the liquid-liquid and resin column extraction efficiency and effectiveness need to be studied.

- The suitability of other solvents in the application of the LLE technique needs to be investigated.

- Spiking techniques need to be developed.

- Material adsorption and blank problems associated with the resin extraction techniques need to be addressed.

- Intercomparison studies of the LLE and resin extraction techniques need to be carried out under field conditions.

- Investigation of the effects of different pretreatment techniques for handling particulate matter (e.g. filtration vs. centrifugation) needs to be conducted and compared in the application of the LLE and resin extraction techniques.

Preconcentration of Trace Organic Compounds From Large Volumes of Water

Registration

J. Lawrence	NWRI, Burlington	(416)336-4927
A. Demayo	WQB, Ottawa	(819)997-3423
V. Niemela	WQB, Ottawa	(819)997-1920
C. Bolton	NWRI, Burlington	(416)336-4707
E. Nagy	NWRI, Burlington	(416)336-4685
F. Philbert	WQB, Ont. Region, Burlington	(416)336-4663
M. Forbes	NWQL, Burlington	(416)336-4577
S.H. Noh	Zenon Environmental Inc. Burlington	(416)639-6320
S. Suter	Ministry of the Environment, Laboratory	(416)235-5895
D. Hall	Ministry of the Environment, Laboratory	(416)235-5910
P. Crozier	Ministry of the Environment, Laboratory	(416)235-5911
J. Doull	WQB, Moncton	(506)857-7842
J-G. Zakrevsky	WQB, Saskatoon	(306)975-5389
H.J. O'Neill	WQB, Moncton	(506)857-7845
Duane McNaughton	NHRI, Saskatoon	(306)975-5735
D. Warry	WQB, Ontario Region, Burlington	(416)336-4641
I. Sekerka	NWRI, Burlington	(416)336-4657
J. Lechner	NWRI, Burlington	(416)336-4657
R. Wilkinson	NWRI, Burlington	(416)336-4657
J. Fischer	WQB-OR, Burlington	(416)336-4961
F.E. Roy	NWRI - RSD, Burlington	(416)336-4903
C.H. Chan	WQB, Burlington	(416)336-4960
Serge Metikosh	WQB-OR, Burlington	(416)336-4963
G. Kan	WQB - Vancouver	(604)987-3543
J.L. Seeley	NWQL - WRD, USGS, Denver, Colo.	(303)236-5345
Dave Rickert	U.S. Geological Survey, Reston, VA	(703)648-6864
B.K. Afghan	NWQL, Burlington	(416)336-4661
Guy LeBel	Health & Welfare Canada, Ottawa	(613)957-1649
A. Sylvestre	WQB-OR,Burlington	(416)336-4966
R. McCrae	WQB-OR, Burlington	(416)336-4642
E. Harrison	Zenon, Burlington	(416)639-6320
B. Brownlee	NWRI, Burlington	(416)336-4706
A. Germain	WQB-QR, Longueuil	(514)646-6043
R. Kwiatkowski	WQB-HQ, Ottawa	(819)997-3422
M. Charlton	NWRI, Burlington	(416)336-4758
K.W. Kuntz	WQB-OR, Burlington	(416)336-4965
S.J. Eisenreich	University of Minnesota	(612)625-3082-5522
P.D. Goulden	NWRI, Burlington	(416)336-4658
I. Suffet	Drexel Univ.	(215)895-2270
Ron Pierce	WQOD/WQB-HQ	(819)953-1553

Doc. No. 3420h

WORKSHOP

PRECONCENTRATION OF TRACE ORGANIC COMPOUNDS
FROM LARGE VOLUMES OF WATER
DRAFT PROGRAM

PURPOSE

Review the performance of preconcentration techniques for the determination of trace organic contaminants in water.

PLACE AND DATE

CCIW, Burlington, Tuesday, June 23, 1987, 8:00-16:30, Seminar Room, 2nd floor

TOPICS

. Liquid - liquid extraction
. Solid - liquid extraction

Uses, limitations, problems, future

PROGRAM	Chairpersons	
MORNING	A. Demayo, B.K. Afghan	
Introduction		
National Water Research Institute and Water Quality Branch	J. Lawrence	08:00 - 08:10
Reviews		
1. Liquid-liquid extraction	P. Goulden NWRI, Burlington	08:10 - 08:45
2. Solid-liquid and liquid-liquid extraction	M. Suffet Drexel University	08:45 - 09:20
Applications		
3. Analysis of drinking water	G. LeBel, H&WC	09:20 - 09:35
4. Preconcentration of organic compounds from large volumes of water	S. Suter MOE-Ontario	09:35 - 09:50
5. Extraction of trace organics with Amberlite XAD-7 and Sephadex A-25	G. Kan, WQB	09:50 - 10:05
Coffee		10:05 - 10:45

Application (continued)

6. Calibration and evaluation of Westfalia centrifuge - Seastar sampler system	A. Germain, WQB, Quebec Region	10:45 - 11:00
7. Development of an automated continuous flow field sampler for trace organic contaminants in surface and ground waters	E. Harrison Zenon Environmental Inc.	11:00 - 11:15
8. Sampling and extraction of large volume water samples for trace organic analysis	K. Kuntz, WQB, Ontario Region	11:15 - 11:30
Discussion		11:30 - 11:45
Lunch		11:45 - 12:45

Afternoon
Review

9. Solid - liquid and liquid-liquid extraction of precipitation samples	S. Eisenreich University of Minnesota	12:42 - 13:20

Applications (continued)

10. Solvent extraction of precipitation samples	C.H. Chan, WQB Ontario Region	13:20 - 13:35

The presentations will focus on the performance of various techniques/instruments, supported by hard data and field experience, in their use for routine monitoring of trace organic compounds in water.

Open Discussion
Moderators: J. Lawrence, F. Philbert 13:35 - 15:00

Coffee 15:00 - 15:30

Conclusions 15:30 - 16:30

REPORT

A report containing abstracts of the presentations and a summary of the afternoon session will be prepared and sent to all participants.